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A study was performed to evaluate the EPA Method 5 procedure for measurement of particulate emissions from a cement kiln. The program included three series of experiments to study the effects of anisokinetic sampling, sampling system temperature, filter size, and nozzle configuration on particulate mass emission determinations. Method 5 was compared with two types of in-stack filters in a fourth set of experiments. The results of the experiments were analyzed by statistical analysis to assess the significance of the sampling system variables on observed differences in collected particulate mass. Chemical and physical characterizations were performed to evaluate the representativeness of collected particulates and to elucidate the cause of mass differences introduced by various sampling system operating parameters.

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EVALUATION OF STATIONARY SOURCE PARTICULATE MEASUREMENT METHODS

VOLUME I, PORTLAND CEMENT PLANTS

by

J. E. Howes, Jr., R. N. Peaut, and W. M. Henry

Battelle, Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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EPA Project Officer: Dr. Kenneth T. Knapp

Chemistry and Physics Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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ABSTRACT

A study was performed to evaluate the EPA Method 5 procedure for measurement of particulate emissions from a cement kiln. The program included three series of experiments to study the effects of anisokinetic sampling, sampling system temperature, filter size, and nozzle configuration on particulate mass emission determinations. Method 5 was compared with two types of in-stack filters in a fourth set of experiments. The results of the experiments were analyzed by statistical analysis to assess the significance of the sampling system variables on observed differences in collected particulate mass. Chemical and physical characterizations were performed to evaluate the representativeness of collected particulates and to elucidate the cause of mass differences introduced by various sampling system operating parameters.

The data show that sampling system temperature is probably the most critical factor in application of the current Method 5 procedure (December 23, 1971) to particulate emission measurements from cement kilns. With the probe and filter temperatures specified in Method 5, ammonium sulfate and/or ammonium bisulfate precipitated in the probe giving high and variable weights of collected particulates. Operation of the sampling probe with a gas outlet temperature of about 205C (400 F) and the filter box of 121C (250F) eliminated the formation of ammonium sulfates in the sampling system.

Anisokinetic sampling at 0.7 and 1.3 times the isokinetic rate and the use of two different nozzle configurations, gooseneck and 90°, did not produce statistically significant differences in particulate mass measurements. Filter size variation produced a significant effect, possibly due to reaction with sulfuric acid in the emissions.

Tests with in-stack flat filters yielded results which were not significantly different from values obtained with the Method 5 procedure modified by using 205 C (400 F) probe and 121 C (250 F) box filter temperature. Results obtained with Munktell in-stack glass fiber thimbles (marketed by Carborundum Co.) were about 18 percent higher than Method 5 values. The difference is shown to result from extraneous sulfate formation in the Munktell thimble. Analyses of Method 5 filters and particulate catches also indicate some reaction of sulfur oxides with MSA 1106BH filter medium.

This report is submitted to the Environmental Protection Agency by Battelle Columbus Laboratories as partial fulfillment of Contract No. 68-02-0609. The work reported in this document was completed on February 28, 1975.

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Dr. Ken Knapp, EPA Project Officer is acknowledged for his guidance and direction of this program.

CONCLUSIONS

The following conclusions regarding methodology for determining particulate emissions from cement kilns may be drawn from this study:

Sampling System Temperature

- The operation of the sampling system at temperatures above the currently specified minimum has a significant effect on the particulate mass data. Operation of the Method 5 sampling train with a filter box temperature of 121 C (250 F) and the minimum specified gas temperature at the probe exit, 121 C (250 F), yielded mean particulate emission values in two test series which were 33 and 43 percent higher than values obtained with the sampling system maintained at the same temperature as the stack gas, about 205 C (400 F). Analysis of the two statistically designed test series shows that the differences are due to system operating temperature and that the effect is significant at confidence levels as high as 98 percent. The difference in results is attributed to formation of ammonium sulfate and/or ammonium bisulfate in the probe operated at a gas exit temperature of 121 C (250 F), from ammonia and sulfuric acid in the source emissions.

- Operation of the Method 5 sampling train with a filter box temperature of about 121 C (250 F) and the gas temperature at the probe exit of about 200 C (392 F) (-80 degrees Centigrade higher than the above test) gave particulate mass emission results which were the same as results obtained with the box filter and probe outlet gas temperature of about 200 C (392 F). The high formation of ammonium sulfate or ammonium bisulfate in the probe or other components of the system was not detected at either of the latter temperature conditions.

Anisokinetic Sampling

- Particulate sampling at about 0.7 and 1.3 times isokinetic flow rate produced particulate mass emission values which were an average 9.9 percent higher and 11.5 percent lower, respectively, than results obtained under isokinetic sampling conditions. The mean mass diameter (MMD) of the cement kiln emissions (after precipitator) was about 0.6 micrometer as determined from in-stack collections analyzed by electron microscopy. Although the observed differences result in estimated confidence levels as high as 70 and 85% in the statistical analysis, usual statistical interpretations of these types of analysis do not declare significant differences until the confidence level exceed a much higher specified level - usually 95 or 99%. Thus, based on the higher confidence level criteria, it is concluded that the observed differences are not statistically significant.

Filter Size

- The particulate mass emission measurements obtained with a nominal 9.4-cm (3.5-in.) filter in the Method 5 train are an average of 8.5 percent lower than results obtained using a nominal 10.2-cm (4-in.) filter. Based on a statistical test of the data, it is concluded with confidence levels as high as 96 percent that the difference which resulted from the two filter sizes is significant. The specific reason(s) for the effect of filter size was not identified but may result from reaction of SO_3 (different filter area), filtration efficiency, or difference in performance due to filter holder design.

Nozzle Configuration

- The use of a goose-neck and smooth 90° nozzle in a Method 5 sampling train did not produce a statistically significant difference in particulate mass emission results. The mean difference of particulate measurements made with the two nozzle configurations is about 1.6 percent.

Filter, Nozzle, and Temperature Interactions

- Statistical analysis of data derived from a confounded factorial designed experiment indicates that interaction effects between temperature (121 and 205 C), filter size (6.4 and 10.2 cm), and nozzle configuration (goose-neck and smooth 90°) did not produce significant differences in particulate mass measurements.

Filter Type and Location

- Sampling with Munktell in-stack glass fiber thimbles gives particulate mass emission values which are an average of 17 and 18 percent higher than values obtained with in-stack, flat, glass fiber filters and with Method 5 (operated with gas temperature of ~205C), respectively. The in-stack, flat, glass fiber filter system (filter and nozzle catch only) yields particulate mass measurements which are an average 0.8 percent higher than Method 5 results. The difference between results obtained with the Munktel thimble and with the in-stack flat filter or Method 5 is statistically significant at a confidence level as high as 99 percent. The confidence level for the in-stack flat filter and Method 5 difference is not sufficient to declare that the two methods give significantly different particulate mass emission results.
- The reaction of SO_3 or H_2SO_4(g) with the Munktell in-stack glass fiber thimble (marketed by Carborundum) yields sulfates which accounts for the differences between the thimble and the in-stack flat filter and Method 5 results.

- Chemical analyses of filters and filter catches indicate that SO_3 or H_2SO_4(g) may also react with MSA 1106 BH glass fiber filter medium when used both in-stack and in the Method 5 configuration. In-stack and Method 5 particulate mass results may be from 10 to 15 percent high due to the sulfate formation.

Method 5 Precision

- The within-laboratory precision (repeatability) of particulate mass emission measurements by Method 5 when performed with a filter box temperature of 121 C (250 F) and a probe outlet temperature of about 205 C (400 F) is estimated to be about 5.5 percent. The estimate was derived from fairly steady state, fixed point measurements; therefore, any errors due to stack traversing and its associated variables (stack temperature, velocity pressure, and movement of equipment) would not be included in the precision estimate.

RECOMMENDATIONS

Based on the conclusions given in the preceding section, the following modifications are recommended to specifically adapt the Method 5 procedure (and similar procedures) to determination of particulate mass emissions from cement plants (kilns). (Many of these recommendations may also be applicable to particulate mass measurements from other types of stationary sources.)

Sampling System Temperature

In order to prevent ammonium sulfate and/or sulfuric acid condensation

- Operate the filter box at a minimum temperature of 121 C (250 F).
- Heat the probe to maintain the gas sample above the temperature of ammonium sulfate and/or sulfuric acid condensation throughout the entire system up to the box filter outlet. Based on this study a minimum gas sample temperature of 191 C (375 F) is suggested for general application of Method 5 to cement plants.
- Sample gas temperature should be measured on the outlet side of the box filter frit with a thermocouple or metal thermometer immersed in the gas stream. Probe heating should be regulated to give recommended operating temperature.

Isokinetic Sampling

Sampling data on a well-controlled source show that deviations of 0.7 and 1.3 times isokinetic sampling rate do not produce a statistically significant difference in mass measurements. The current Method 5 requirement for a valid performance test limits the maximum deviation to the range 0.9 to 1.1 times isokinetic sampling rate. For current and future well-controlled cement kilns, emissions, isokinetic sampling deviations within the specified range should not produce a significant error in particulate mass measurements.

The study results suggest that the permissible range of isokinetic sampling deviation could be extended without adverse effects. However, normal cement kiln operating characteristics do not impose any problems in maintaining sampling rates within the specified range of ± 10 percent.

- Consequently, no changes are recommended in the acceptable isokinetic sampling rate deviation range set forth in Section 6.6 when Method 5 is used for cement plants.

Filter Size

- Additional investigation is suggested to study the effect of filter size (area) on particulate mass gain. A study of SO_3 or H_2SO_4(g) reaction with the MSA 1106 BH filter medium (also suggested in a subsequent section) may provide an explanation.
- From a performance standpoint, a nominal 7.6-cm (3-in.) filter holder of the type used in this study is recommended for Method 5 sampling. The filter area is sufficient to accept anticipated loadings and ease of handling (assembly, disassembly, and placement in heated filter box) is superior to a similar 10.2-cm (4-in.) filter holder
- The 5.2-cm (2.5-in.) filter holder of the design used in this study is not recommended for use in Method 5. Filter assembly and recovery in a quantitative manner is difficult to perform without extreme care. Damage to the filter can occur from misalignment of the sintered glass frit and its retaining ring. Pressure drop across the smaller filter could also be a problem at higher particulate concentrations.

Nozzle Configuration

- A goose neck nozzle is recommended for the Method 5 sampling train. Separate wind tunnel studies have shown that relative nozzle and pitot tube location is more critical with the 90° nozzle.

Particulate Filter

- The Hunktel glass fiber filter thimble currently marketed by Carborundum is not recommended for particulate sampling of cement kilns.
- The use of an in-stack flat filter with at least a 80.3-cm^2 (3.14-in^2) area is recommended as a suitable alternate to the Method 5 filter configuration.
- Additional study of the reaction of sulfur oxides with filter media is recommended to quantify the extent of extraneous sulfate formation and to select materials which minimize this source of error.

Method 5 Precision

- Specific equipment and procedures for recovery of particulates from the probe should be given in Method 5. The inherent and potential error in this step is probably the most significant in determining the precision of the method.

INTRODUCTION

The Clean Air Act as amended in 1970 provides the impetus for programs to improve the air quality in the U.S. through research to broaden the understanding of the effects of air pollutants, research and development of techniques to control emissions, and the enactment of air quality regulations to protect the public welfare. Pursuant to Section 111 of the Act, the Environmental Protection Agency (EPA) on December 23, 1971, promulgated Standards of Performance for New Stationary Sources (amended) for fossil fuel-fired steam generators, incinerators, portland cement plants, and nitric and sulfuric acid plants[1]". On March 8, 1974, similar performance standards were issued for asphalt concrete plants, petroleum refineries, storage vessels for petroleum liquids, secondary lead smelters, secondary brass and bronze ingot production plants, iron and steel plants and sewage treatment plants[2]. All new and modified sources in the preceding categories are required to demonstrate compliance with the standards of performance.

The performance standards are intended to reflect "the degree of emission limitation achievable through the application of the best system of emission reduction which (taking into account the cost of achieving such reduction) the Administrator determines has been adequately demonstrated"[3].

Compliance with required performance is determined by testing procedures specified with the standards. The use of a procedure called "Method 5 Determination of Particulate Emissions from Stationary Sources"[4] is specified in all instances where particulate mass emission measurements must be made. A copy of the Method as promulgated is given in Appendix A. The Method 5 procedure consists of isokinetic extraction of a sample from the emission stream with a heated probe and collection of the particulates on a heated filter. With the recent exception of fossil fuel-fired power plants[5], the same sampling system operating parameters have been adopted for all stationary sources.

The source categories subject to Method 5 particulate measurements include diverse processes which encompass a wide range of the following emission characteristics; moisture content, gas temperature, gas composition, particulate concentration and composition, and flow dynamics. Interaction of these emission properties with the Method 5 sampling technique can produce significant variations in the results of particulate emission measurements. The following examples of some of the reactions which may affect particulate measurements.

* References are given on page 91.

(1) SO_3 or H_2SO_4 in emissions can condense to form sulfates which increase the mass of collected "particulates". The SO_3-H_2SO_4 dew point is dependent on SO_3 concentration and moisture content of the emissions.

(2) The filter particulate catch may present a surface for reactions with gaseous emission components such as SO_2 and NO_2. Reactivity would be dependent on particulate loading and composition and on gas composition of the emissions.

(3) Changes in gas temperature in the sampling system may alter the apparent particulate concentration through condensation or volatilization.

Such interactions with the sampling process must be recognized and controlled if Method 5 is expected to yield reliable particulate measurements for individual source categories.

The work presented in this report which was performed as part of an EPA program to study the applicability of the Method 5 procedure to measurement of particulate emissions from a variety of stationary sources. Specifically, this work addresses the question of whether Method 5 provides an accurate, reliable measurement of particulate emissions from cement plants. Earlier, an interim report[6] was issued on the preliminary study results. Some data from this earlier report has been included here to present a complete document on the use of Method 5 for sampling cement plant emissions.

OBJECTIVES

The objective of the overall EPA program is the evaluation of the applicability and reliability of Method 5 (conducted as specified in the Federal Register, December 23, 1971) for the determination of particulate mass emissions from stationary sources for which performance standards have been promulgated. The portion of the overall program covered by this report is aimed at evaluation of Method 5 performance when the procedure is applied to cement plants. The study sought to identify any characteristics of the sampling method or unique properties of cement kiln emissions which would adversely affect particulate measurements and, if possible, recommend appropriate corrective measures in sampling methodology.

EXPERIMENTAL WORK AND RESULTS

Experimental Approach

In accord with the program objectives, an experimental plan to evaluate the performance of Method 5 was formulated which included determination of the general emission characteristics of a cement kiln, a study of the parameters of the Method 5 sampling procedure which might affect particulate measurements, and comparison of Method 5 with in-stack sampling techniques. All experiments were performed in statistically designed series to provide the maximum information with a minimum number of experiments and to permit assessment of the statistical significance of observed differences from the factors treated as independent variables.

Initially, the effects of Method 5 sampling system parameters on particulate measurements was studied. These parameters included

- Anisokinetic sampling
- Probe and filter temperature
- Filter size
- Nozzle configuration.

The experiments were intended to reveal the sensitivity of particulate measurements to the sampling variables and to determine if current Method 5 operating parameters are within a range which will produce accurate, reliable results.

Two types of in-stack filters (glass fiber flat and thimble) were compared with Method 5. Particulates collected under in-stack conditions might be considered less subject to compositional alterations, especially by condensation products and reactions which may occur upon cooling below stack temperature assuming stack temperature is greater than 121C(250F). Accordingly, comparison of the in-stack and Method 5 particulate collections provides an approach to the study of sample alterations which may be introduced by the Method 5 sampling procedure. In addition, in-stack collection essentially eliminates deposition of the particulates in probe and facilitates the study of reactions which may occur in the probe, e.g., condensation of H_2SO_4.

Another consideration behind the methods comparison is that EPA is

considering adoption of the in-stack technique as an optional performance test method. Equivalency of Method 5 and the in-stack method must be demonstrated to maintain consistency with established performance standards.

The approach selected to conduct the experimental study consisted of concurrent sampling at approximately the same point in the cement kiln stack with two sampling systems operated under the various conditions under study. Filter and probe collections were analyzed gravimetrically and chemically to detect differences resulting from various sampling parameters. Analyses of the gas composition of the kiln emissions were performed to identify components which might interact with the sampling process. The mass emission data from the experiments were analyzed statistically to determine the significance of observed differences.

The following sections present detailed descriptions of the emission source, sampling equipment and sampling and analysis procedures. In subsequent sections, the experimental test results are then presented and discussed.

Process and Sampling Site Description

Cement Manufacturing Process

The manufacture of portland cement is a basic industry in the United States with a current annual production of about 80,000,000 metric tons. Based on the past few years, production is expected to grow at the rate of about 5 percent per year.

Portland cement is produced from the following raw materials (listed in decreasing order of consumption): limestone (including oyster and clam shell), cement rock, clay and shale , gypsum, marl, sand and sandstone, and blast furnace slag. The production process involves four major steps: quarrying and crushing, grinding and blending, clinker formation, and finish grinding. In production by the dry process, the raw materials are ground, blended, and fed into the kiln (clinker formation) in dry form. In the wet process, water is used in the grinding and blending operations and the raw materials are fed into the kiln as a slurry containing as much as 30 to 40 percent water. In 1972, 62 percent of the 175 plants in the United States manufactured cement by the wet process and 38 percent employed the dry process.

The kiln operation, used in the clinker formation step, is the major source of emissions (both gaseous and particulate) in cement production. The kiln is a rotating steel cylinder, typically 10 to 20 feet in diameter and 300 to 600 feet long, lined with refractory brick. It is mounted horizontally with a slight slope from the upper end at which raw materials are introduced to the lower end through which the clinker exits and the kiln is fired. Coal, fuel oil, or natural gas may be used as fuel for the kiln.

The drawing in Figure 1 illustrates the main features of the kiln operation. The raw materials are fed into the upper end of the gently sloped, rotary kiln and flow slowly toward the lower, increasingly hotter end of the kiln. In passage, the charge is dried, calcined and finally at a point of incipient fusion forms a substance called clinker. The clinker is cooled, ground, intermixed with gypsum to produce the finished product.

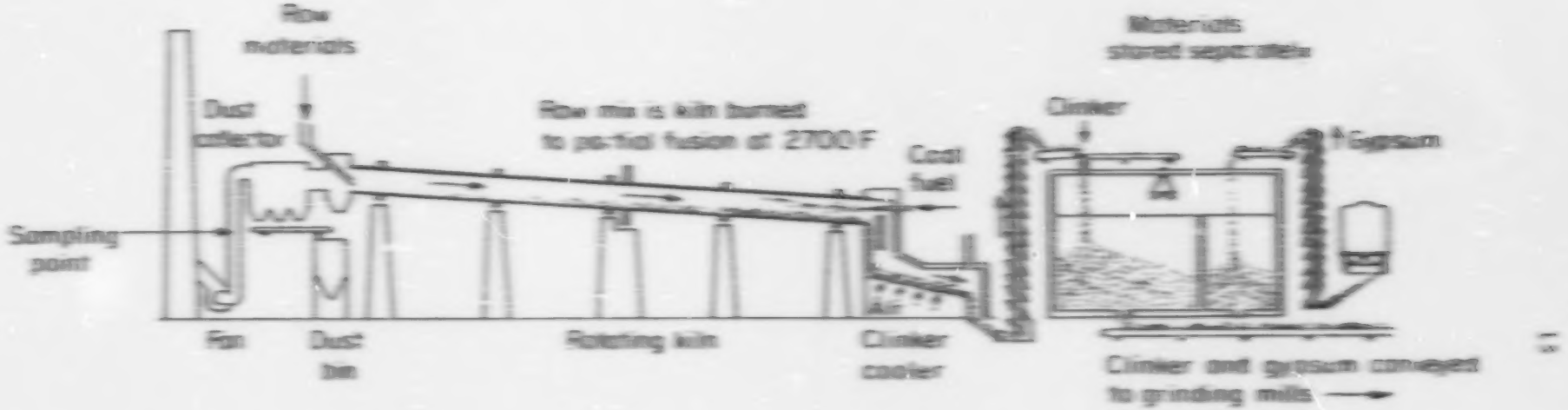


FIGURE 1. KILN OPERATION OF PORTLAND CEMENT PRODUCTION

The combustion products and excess air pass through the kiln countercurrent to the raw material flow carrying with them reaction gases from the calcination process (principally CO_2), moisture, and dust particles from throughout the kiln. The dust loadings generated by the kiln operation, which are reported to range from 1 to 33 percent of the finished product[7], require a control device such as an electrostatic precipitator or baghouse to comply with current emission regulations.

Sampling Site Description

All sampling experiments conducted as part of this study were performed at the Columbia Cement Corporation, Zanesville, Ohio. This plant operates two rotary kilns and produces in excess of 3,000,000 barrels of cement per year by the wet process. The principle raw feed materials are limestone and shale and the kilns are fired with pulverized coal which contains about three percent sulfur. The emission of particulate material from the kilns is controlled by recently installed electrostatic precipitators.

Sampling was performed in a vertical run of duct carrying emissions from kiln #5 precipitator outlet to the stack discharge blower. The point of sampling is indicated on the drawing presented in Figure 1. The duct at the sampling location, a large platform beneath the precipitators, contains six sampling ports arranged as shown in Figure 2. A temperature and velocity head (ΔP) profile of the stack cross section at the sampling ports is presented in Figure 3.

The general emission characteristics of the kiln are summarized in Table 1. Carbon dioxide in the emissions results from decarbonation of the limestone as well as from combustion. Lower SO_2 levels had been anticipated based on previous information[7]. Significant variations were observed in SO_2 emission levels as will be noted from continuous monitoring data presented later in this report. The flow through the kiln was relatively constant. Gas temperatures variations of about 22 degrees centigrade (40 F) were observed during some of the two hour testing periods. Both gas temperature and SO_2 variations are associated with coal firing rate changes which are required to maintain the charge (fused mass) in the proper zone of the kiln.

FIGURE 2. SAMPLING PORT LOCATION IN DUCT LEADING FROM PRECIPITATOR TO STACK

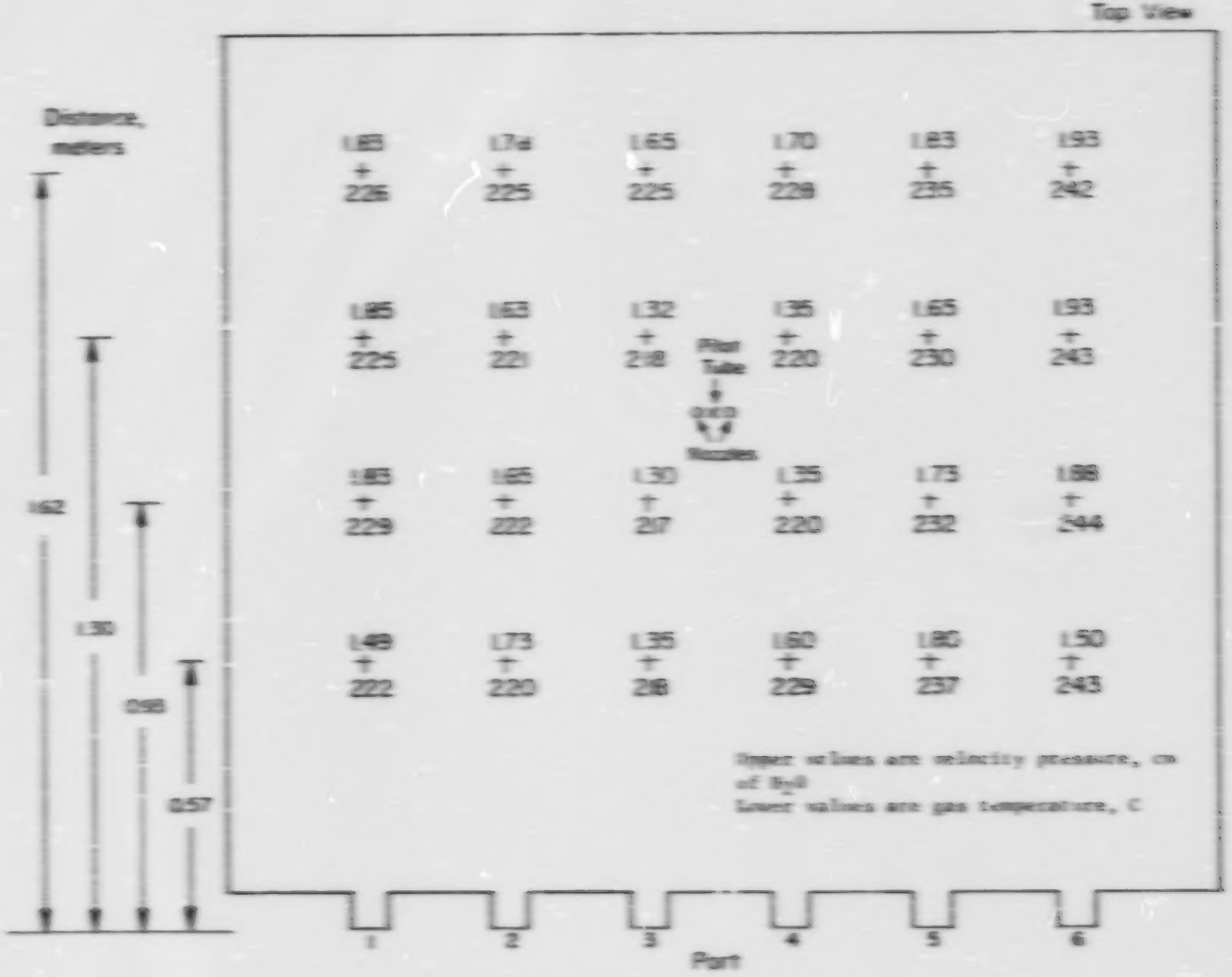


FIGURE 3. VELOCITY PRESSURE AND TEMPERATURE PROFILE OF CEMENT KILN EMISSION DUCT AT SAMPLING LOCATION

TABLE 1. EMISSION SOURCE CHARACTERISTICS

Composition of Kiln Emissions	
Particulates	~23 mg/Nm^3 (~0.01 grain/SCFD)
CO_2	~19 percent, dry basis
O_2	~8 percent, dry basis
N_2	~73 percent, dry basis
SO_2	~450 ppm (Average)
NO_x	~535 ppm (Average)
Moisture	~30 percent
Flue Gas Conditions	
Temperature	188 to 236 C (370 to 457 F)
Volumetric Flow	1,473 m^3/min, Dry (~52,000 DSCFM)
Average ΔP	1.65 cm (0.65 in.) H_2O
Static pressure	2.1 cm (0.81 in.) Hg, negative
Flue and Port Dimensions	
Flue Size	1.83 m x 2.13 m (6 ft x 7 ft)
Port diameter	7.62 cm (3 in.)

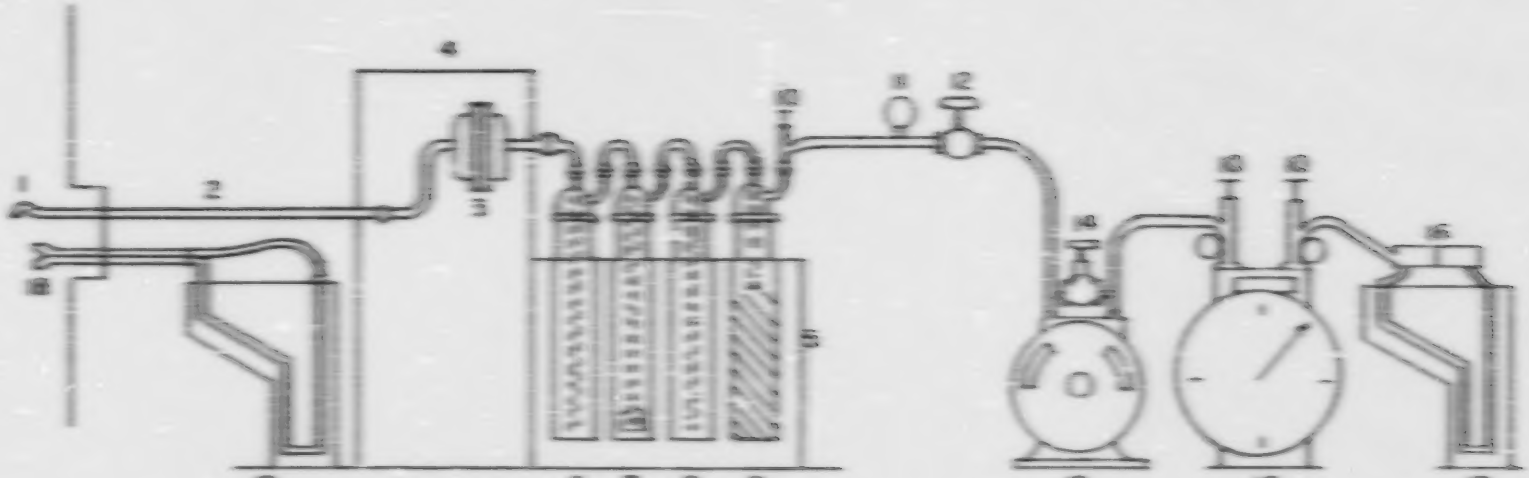
Sampling Equipment

Particulates

The particulate sampling was performed with two identical Method 5 trains comprised of components connected as shown schematically in Figure 4. The control module and impinger box assembly of the systems, shown in Figure 5, are commercially-built units. The sampling probes, which were constructed at Battelle, were 2.06 m (6.8 ft) in length and were constructed from approximately 11-mm-ID x 15-mm-OD glass tubing. Heating was provided by a 3.05-m (10-ft) glass fiber-insulated heating tape wrapped around the glass probe. A thermocouple junction was taped to the outer surface of the glass tubing at a point between the heater windings and at the midpoint of the probe. The glass probe and heating tape assembly was insulated by a wrapping of asbestos tape. A stainless steel sheath was used to protect the glass probe and to hold the fitting to attach the nozzle. The seal between the glass probe and the 1.6 cm (5/8 in) Swagelok® nozzle connection was made with a silicone O-ring.

A single type "S" pitot tube attached to one of the sampling probes was used for velocity head readings. The tube was constructed at Battelle from approximately 7.5 mm I.D. x 9.5 mm O.D. stainless steel tubing. A stainless steel sheathed thermocouple was attached to the pitot tube to provide stack temperature measurements. A photograph showing the pitot tube sensing head and the position of the thermocouple is presented in Figure 6. The type "S" pitot tube was calibrated against a standard pitot tube over the velocity range of 10.7 to 29.6 m/sec (35 to 96 ft/sec) in the Battelle wind tunnel facility.

Modifications and variations to the "normal" Method 5 sampling train were made for several test series to study sampling methodology. These are described in the following sections.



1. Stainless steel nozzle
2. Glass-lined probe
3. 7.62 cm (3 in) filter
4. Heated box for filter
5. Ice bath for impingers
6. Modified G-S impinger with 100 ml water
7. Greenburg-Smith impinger with 100 ml water
8. Modified G-S impinger
9. Silica gel trap
10. Thermometers or Thermocouples
11. Vacuum gauge
12. Flow control valve
13. Pump
14. Flow control valve
15. Dry test meter
16. Calibrated orifice
17. Manometer (ΔH)
18. "S" type pitot tube
19. Manometer (ΔP)

FIGURE 4. SCHEMATIC DIAGRAM OF METHOD 5 TRAIN
USED FOR SAMPLING CEMENT KILN EMISSIONS

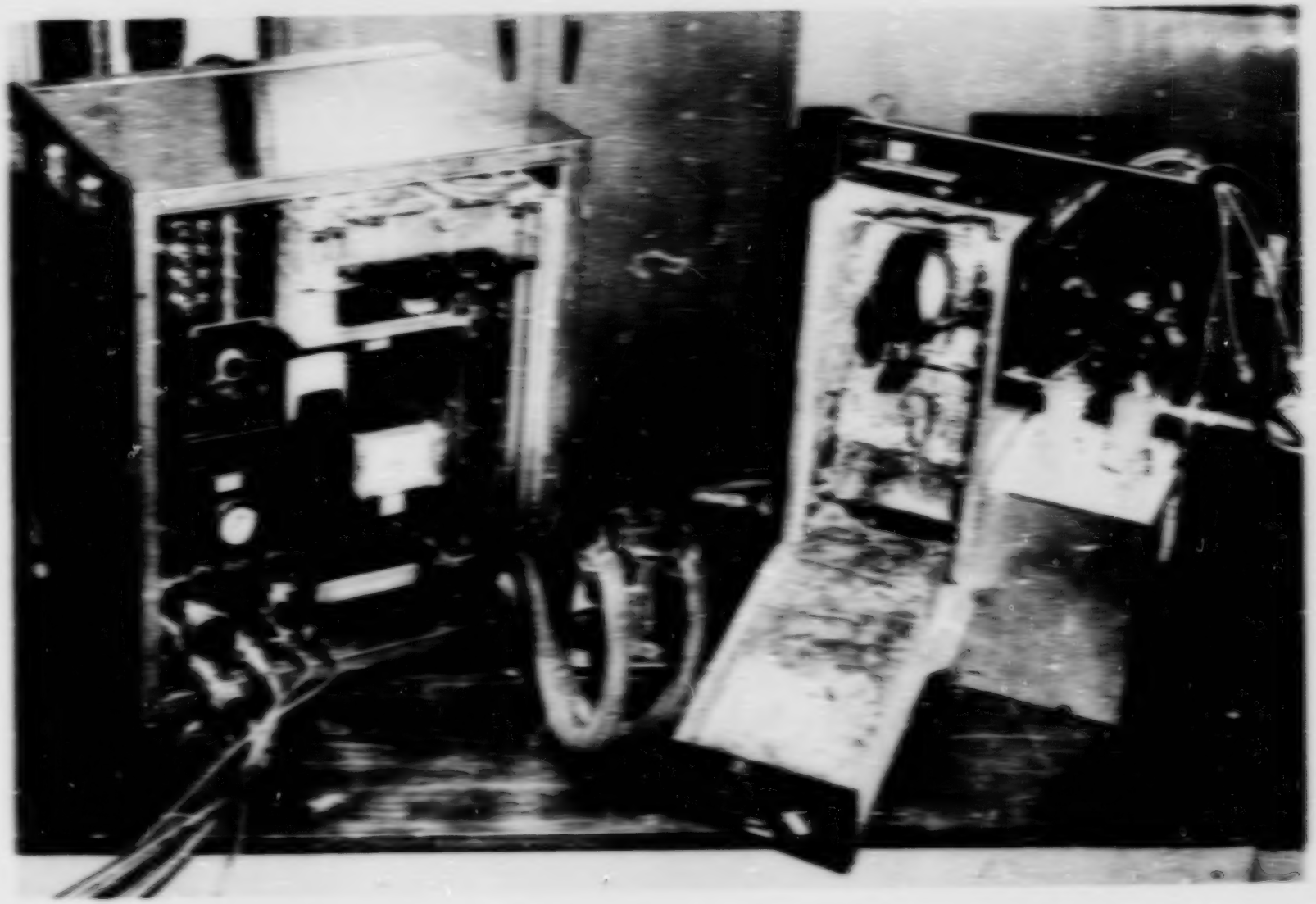


FIGURE 1. EQUIPMENT USED FOR SAMPLING PARTICULATES IN CEMENT PLANT EMISSIONS

FIGURE 6. PITOT TUBE HEAD AND THERMOCOUPLE USED FOR VELOCITY HEAD AND STACK TEMPERATURE MEASUREMENTS

Temperature Measurements. The glass connectors from the probe outlet to the filter and the filter outlet to the first impinger were modified to permit additional measurements of gas sample temperature. Figure 7 shows the modified connector used in all tests to measure and control gas temperature at the probe outlet. The connector contains a thin-wall thermocouple well which extends about 5.1 cm (2 in.) into the outlet end of the probe. Figure 8 shows the modified connector used in some tests to obtain gas temperature measurements at the filter outlet. The tip of the metal thermometer was positioned about 1.3 cm (0.5 in.) from the frit in the filterholder.

Nozzles. The two types of nozzles shown in Figure 9 were used in a study of the effect of nozzle configuration. The nozzles were formed from approximately 7.5-mm-ID x 9.5-mm-OD stainless steel tubing and the sampling tips were machined to a knife edge with a 7.7 mm (0.303 in.) diameter opening. The goose neck type nozzles were used on both sampling systems in all tests with the exception of the experiments to study nozzle configuration.

Filterholders. The 6.25 cm (2.5 in.) and 10.2 cm (4 in.) filterholders shown in Figures 10 and 11, respectively, were used in the experiments to study the effect of filter size. The silicone rubber ring shown with the 6.25 cm filter was not used because it stuck to the glass fiber filters.

A 7.6 cm (3 in.) filterholder of the design shown in Figure 11 was used in all other tests with the Method 5 train and as the back up filter in tests in which an in-stack filter was used.

FIGURE 7. THERMOCOUPLE ASSEMBLY USED TO MEASURE GAS TEMPERATURE AT PROBE OUTLET

FIGURE 8. THERMOMETER ASSEMBLY USED TO MEASURE GAS TEMPERATURE AT THE BOX FILTER OUTLET

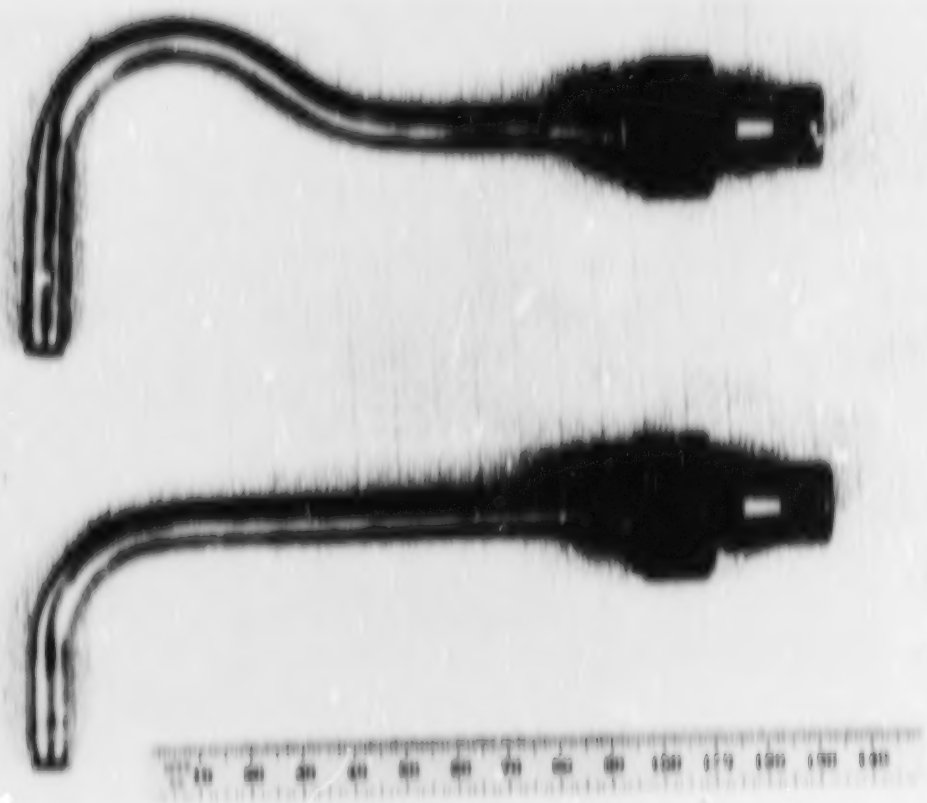


FIGURE 9. SAMPLING NOZZLES

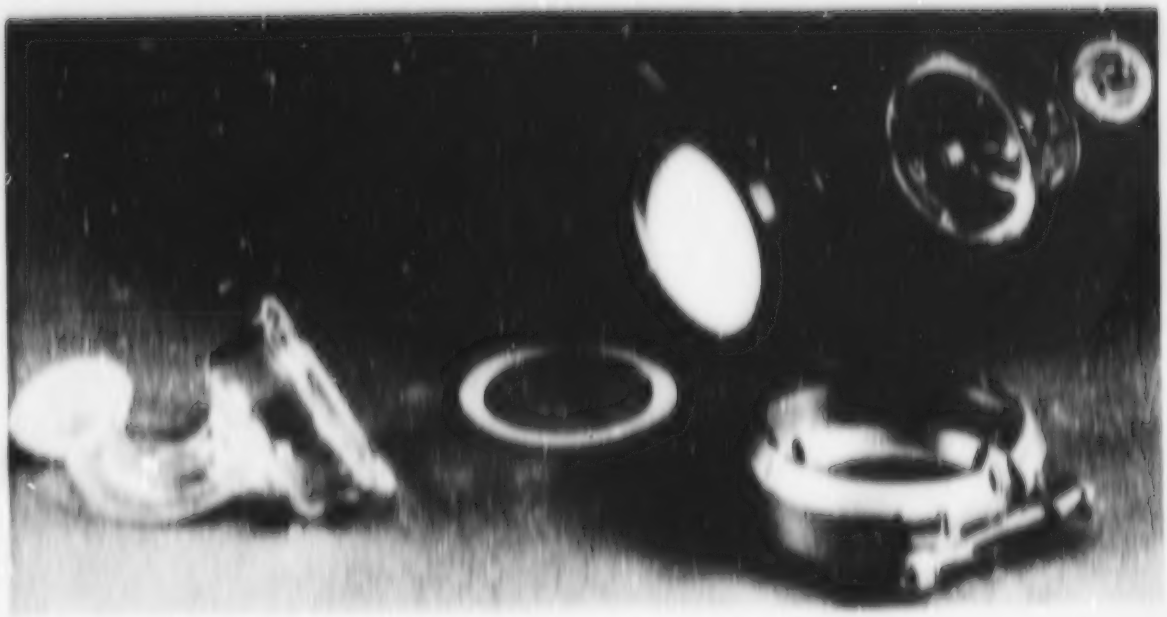


FIGURE 10. OUT-OF-STACK FILTER HOLDER FOR 6.35-CM-DIAMETER FILTERS

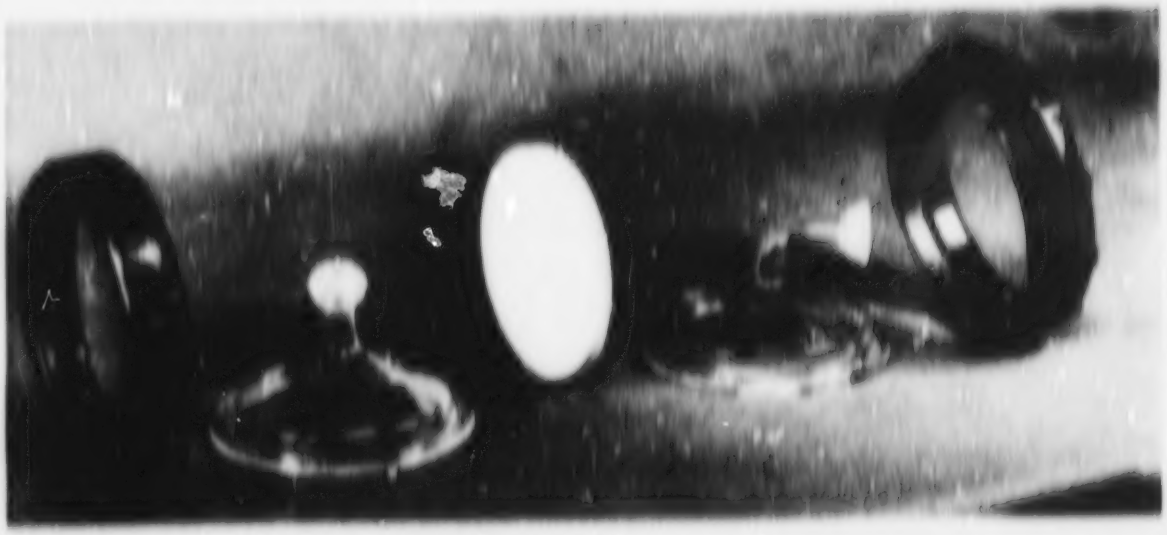


FIGURE 11. OUT-OF-STACK FILTER HOLDER FOR 10.1-CM-DIAMETER FILTERS

The two types of filter holders used for in-stack sampling are shown in Figures 12 and 13. The 6.35 cm (2.5 in) holder for flat filters shown in Figure 12 is a commercially-available unit. The actual filtration area is about 25.7 cm^2 (4.0 in^2).

The in-stack filterholder shown in Figure 13 was constructed at Battelle and was designed to use Hunktell glass fiber thimbles which are marketed by Carborundum Co.* The thimble was sealed to the inlet with the spring-loaded, stainless steel collar and a Teflon® gasket was used to seal the filterholder body.

Both in-stack filterholders were equipped with fittings to connect them between the probe and the goose neck nozzle described previously.

Filter Materials. Mine Safety Appliance (MSA) 1106 BH glass fiber filter medium was used in all flat filter applications, both out-of-stack and in-stack, and Hunktell glass fiber thimbles were used for some in-stack particulate collections. An analysis of these filter materials obtained by optical emission spectroscopy is given in Table 2. Analyses of some alkali metal and alkaline earth elements which can be removed from the filter media by leaching with hot 0.1 N HCl are presented in Table 3. Table 4 gives the results of pH analyses obtained by TAPPI Method T435 su-68[8] and alkalinity analyses performed according to ASTM Method D202[9].

Gas Analysis

Continuous monitoring for SO_2 and NO_x was performed during the preliminary cement plant sampling study by an Environmetrics Model NS 300 AC Paristor unit. The gas sample was extracted from the duct through a 0.63 cm (0.25 in) diameter stainless steel tube and passed through a moisture trap prior to the Paristor unit. Teflon® lines were used to connect the monitor to the sampling probe.

*Hunktell's Swedish filter paper is made by Gryckebo Pappersbruk, AB, Sweden.

FIGURE 12. IN-STACK FILTER HOLDER FOR 6.25-CM-DIAMETER FILTERS

FIGURE 13. IN-STACK FILTER HOLDER FOR GLASS FIBER THIMBLES

TABLE 2. COMPOSITION OF FILTER MATERIALS

Filter Type	Element Composition, weight percent								
	Si	Na	Ca	K	Ba	Al	B	Fe	Mg
[illegible]	Major	3-6	4-7	1-2	0.02	2-4	1-2	0.1	1.0
[illegible]	Major	3-6	1-2	2-3	2-4	2-4	1-2	0.05	0.05

	Sn	Pb	Cu	Zn	Ti	Zr	Mn	Sr	Cr
[illegible]	0.002	< 0.005	< 0.001	< 0.02	0.005	0.005	< 0.001	0.02	0.005
[illegible]	0.005	0.02	0.005	2-4	0.01	0.005	< 0.001	0.1	0.003

TABLE 3. ANALYSIS OF AVAILABLE ELEMENTS[a]

Element	Availability of Elements[b] [c]			
	Milligrams/Filter		Approx % of Total in Filter	
	MSA 1106 BH	Thimble	MSA 1106 BH	Thimble
Ba	<0.02	3.8	--	12
Ca	0.12	1.6	0.7	6
K	0.1	3	3	8
Na	1.5	13	12	17
Zn	0.006	4.1	--	8

(a) Leached from filter materials with hot 0.1N HCl.

(b) MSA 1106 BH = 8.26 cm (3.25 in) dias
Thimble = Munktell (Carborundum)
Results are the average of two determinations

(c) Analyses performed by atomic absorption

TABLE 4. pH AND ALKALINITY OF FILTERS

Filter Type[a]	pH	Alkalinity[b]
MSA 1106 BH - A	9.60	0.088
- B	9.35	0.077
Munktell (Carborundum) - A	9.35	0.117
B	9.10	0.123

(a) A and B represent analyses of two different filters of each type. MSA filter size = 8.26 cm (3.25 in.) diameter.

(b) Milliequivalent of acid required to neutralize the alkalinity of leach solution.

Analyses for CO_2 and O_2 were determined with Orsat and Fyrite equipment. Nitrogen was assumed to comprise the balance of the emission gas mixture.

Ammonia in the kiln emissions was determined by sampling with a Method 5 train in which 150 ml 1M sulfuric acid was used in the first and second impingers in place of water.

Sulfur oxides were determined by the Gokéyr-Ross method[10]. The sampling system consisted of the particulate sampling probe with a modified nozzle to hold a quartz wool filter, a temperature controlled condenser to collect sulfuric acid, and two serially connected Greenburg-Smith impingers containing hydrogen peroxide to trap SO_2. The system is similar to the equipment described in ASTM Method D 3226-73T[11].

Sample Collection and Analysis Procedures

Particulate Sampling

In all tests, particulate sampling was performed concurrently with two systems (designated A and B), each with a separate operator. The systems as employed for sampling at the test site are shown in Figure 14. Sampling system equipment and operating conditions used in the tests were varied in accordance with statistically designed experimental patterns.

All sampling was performed at a fixed-point at the center of the duct in an area of nearly uniform velocity. Sampling probes of the two systems were inserted at a slight angle into the duct through two adjacent ports so that the pitot tube attached to one of the probes was positioned equidistance between the sampling nozzles. The separation between the pitot tube and each nozzle was about 2.5 cm (1 in.). The relative nozzle-pitot tube position and the point of sampling within the duct are indicated in Figure 3.

At the start of each test day, the laboratory calibration of the gas metering components of both sampling systems was checked by setting the orifice manometer (ΔH) to the meter box calibration factor ($\Delta H_@$) and measuring the flow rate through the dry gas meter over a 5-minute period. A flow rate of 0.021 m^3/min (0.75 cfm) confirmed that the gas metering system remained in calibration.

The preparation of the particulate collection trains for all tests was performed as specified in Paragraph 4.1.2 of Method 5 with the following modifications:

(1) The entire sampling train was leak checked by plugging the sampling nozzle inlet and evacuating to 38.1 cm (15 in.) of Hg. Leak rates did not exceed 566 cm^3/min (0.02 cfm). This procedure was used for both the regular Method 5 train and the in-stack filter train. Prior to leak testing, the in-stack filter assembly was heated with a 260-399 C (500-750 F) heat gun. Heating was continued until the probe was inserted into the duct to initiate sampling.

Impinger Boxes

Meter Boxes

FIGURE 14. CONCURRENT SAMPLING AT TEST SITE

(2) The probe was heated until the thermocouple at the outlet indicated that the desired operating temperature was achieved prior to initiation of sampling.

(3) Heat guns (260-399 C) were used for supplemental heating when the box filter was operated at temperatures above 121 C (250 F).

(4) An additional modified Greenburg-Smith impinger (without water) was required to collect condensed moisture when sampling rates of 1.3 times isokinetic were used.

In performance of the tests, sampling trains were operated as described in Paragraph 4.1.3 of Method 5 with the exception that readings of ΔP, ΔH, stack temperature and sampling system temperatures were recorded at 10-minute intervals. The velocity head (ΔP) for both systems was determined from one pitot tube and nomographs were used to obtain the proper sampling rate (ΔH). Temperature measurements were obtained at the points shown in Figure 15.

The sampling period for each test was 2 hours and total dry gas sample volumes at isokinetic sampling rates ranged from 2.1 to 2.4 m^3 (74 to 85 ft^3).

After completion of the tests, the trains were again leak checked, sealed to prevent contamination, and transferred to the sample recovery area.

Sample Recovery and Analysis

Filters were removed from holders, sealed in Petri dishes or glass jars (thimbles) and immediately placed in a desiccator. For Method 5-type tests, the probe and nozzle were disassembled and washed separately. First, the probe was first rinsed with acetone without brushing, then rinsed with acetone while slowly inserting and removing a Nylon® brush in a rotating fashion. The acetone wash and brushing were continued until visual inspection indicated that all particulates were removed. The brush was thoroughly flushed with acetone prior to removal from the probe. The probe wash (usually about 100 to 150 ml) was collected in an Erlenmeyer

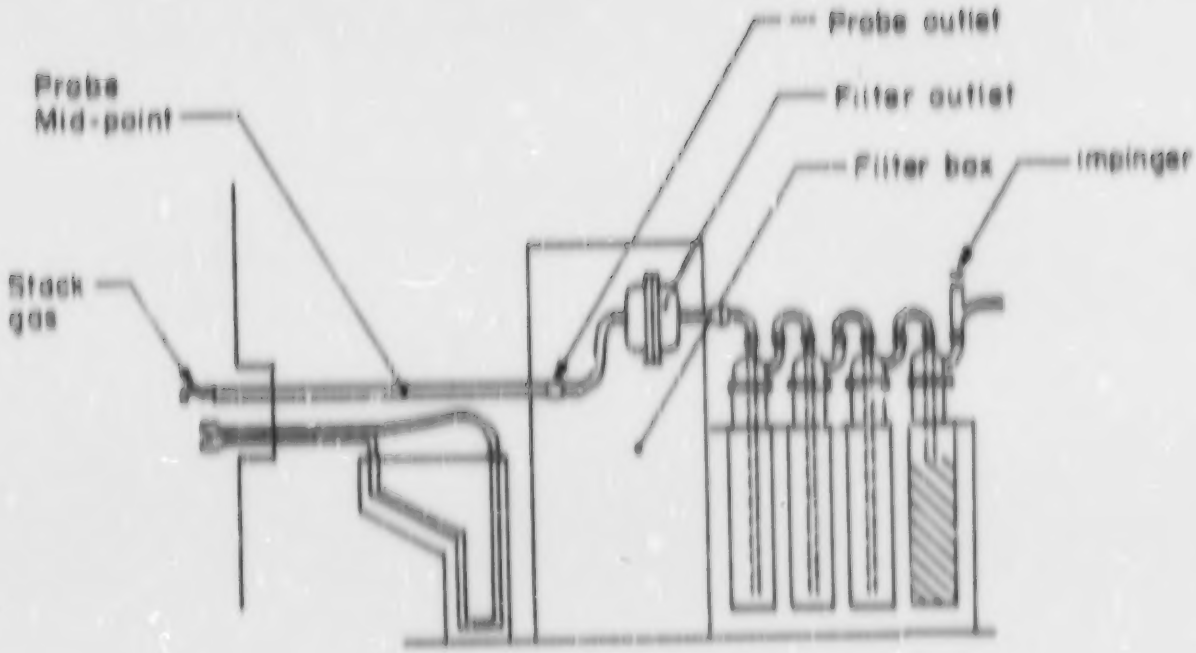


FIGURE 13. TEMPERATURE MEASUREMENT POINTS

flask sealed onto the probe outlet ball joint. Particulates were recovered from the nozzle and the inlet half of the filter holder by alternately brushing and rinsing with acetone. The wash solutions from all three components (probe, nozzle, and filterholder) were combined for analysis.

In tests with in-stack filters, the in-stack filter was removed from the probe and particulates were recovered from the probe as described in the previous paragraph. The outlet side of the in-stack filterholder and in inlet side of the back-up filterholder (box filter) were separately brushed and washed with acetone and the solutions were combined with the probe wash. The nozzle and inlet side of the in-stack filterholder, as one unit, was alternately brushed and washed with acetone. This wash solution was not combined with the probe wash, but analysed separately.

At least one 500 ml acetone blank was obtained each day from the wash bottle dispenser. All acetone wash solutions and blanks were stored in glass bottles with Teflon(R)-lined caps for transfer to the laboratory for analysis.

The MSA 1106 BH filters and particulate catch were desiccated at least 24 hours (usually longer) prior to weighing. It was found necessary to desiccate the Munktell (Carborundum) thimbles at least 72 hours prior to weighing (both tare and final) to achieve a constant weight.

The acetone wash solutions were evaporated to dryness in a reverse airflow, clean hood and the residues were desiccated to a constant weight (usually 24 to 48 hours). Residues and filters were weighed to the nearest 0.1 mg.

Calculations were performed as described in Section 6 of Method 5.

Gas Analyses

Continuous analyses for SO_2 and NO_x were performed concurrently with all tests in the preliminary series of particulate sampling experiments. A gas sample was withdrawn from the kiln emissions at the rate of about 1.5 liters/minute passed through an ice-cooled moisture trap and analysed with an Environmetrics NS300 AC monitor. Periodic calibrations were

performed on-site by passing gas mixtures containing known concentrations of SO_2 and NO through the same intake system.

CO_2 and O_2 analyses by Fyrite or Orsat were performed during each particulate test.

Two ammonia determinations were performed using a Method 5 particulate train operated with a probe outlet gas temperature of 213 C (416 F) and a box filter temperature of 121 C (250 F). Sampling was conducted at the rate of about two liters/minute for 30 minutes in one test and 60 minutes in another. The ammonia was reacted with 1 N sulfuric acid contained in the impinger train and subsequently determined by micro Kjeldahl analysis. Samples of the sulfuric acid solutions used in the impingers were analyzed for ammonia blank.

A controlled SO_3 condensation procedure similar to ASTM D 1326-71T[11] was used to sample for SO_3 and SO_2 (SO_x) in the kiln emission. Sampling was performed for 60 minutes at a flow rate of 2.8 liters/minute with the probe operated at about 205 C (400 F). The sulfuric acid condensation coil was maintained at 82 C (180 F). SO_2 was collected in 3% hydrogen peroxide which oxidized it to sulfate. After sampling, the probe and condensation coil were rinsed with water and the combined solution was analyzed for sulfate resulting from SO_3. The hydrogen peroxide trap solutions were analyzed for sulfate formed from the SO_2. Sulfate analyses were performed by the barium perchlorate-thorin titration method.

Test Descriptions and Results

Four separate test series were conducted in this study to investigate the effects of the following sampling variations on the particulate collection process:

1. Isokinetic versus anisokinetic sampling,
2. Filter size, temperature and nozzle configuration,
3. Filter box and probe temperatures, and
4. Filter types (Method 5 and in-stack).

In designing the statistical plan for each test series, it was necessary to select appropriate patterns in light of the number of simultaneous samples which could be collected and the number of treatment combinations (i.e. combinations of varying levels of experimental conditions) being studied. The sampling environment allowed for the collection of only two simultaneous samples while the various test series involved more than two treatment combinations. Consequently not all treatment combinations could be evaluated simultaneously. Because of the probability that stack conditions would vary over time, experimental designs were selected which permitted statistical adjustments in the collection of the data, so that effects which may have been attributable to differences in controllable factors (i.e., the factors being studied) would not be confounded with variations in the uncontrollable factors (i.e., varying emission rates in the source) over time. Two statistical designs were used.

A Balanced Incomplete Block Design was used for two of the four test series conducted -- the series on effect of filter type and the series on the effect of probe and filter temperature combinations. In each of these series, three treatment combinations were studied in all possible simultaneous pairs. Thus, if the treatment combination levels are denoted by "A", "B", and "C", the statistical pattern for the series required that three pairs of simultaneous samples - (A,B), (A,C), and (B,C) - be collected, with appropriate adjustments in the data for temporal variations in the source emissions.

A Confounded Factorial Design was used for the test series on effect of anisokinetic sampling conditions and for the series on the effects of filter size, sampling system temperature, and nozzle configurations. In this design, treatment combination were assigned to the simultaneous pairs which were collected in such a way that the experimental factors which were of primary interest were not confounded with temporal source variations. This condition was achieved by deliberate confounding of less important factors with the source variations over time, or through partially balanced confounding over replications. That is, with replications of the experimental design, different effects were confounded during each replication so that partial information was available on these factors.

The statistical approach used in analysis of data in this study is the commonly used "analyses of variance", which partitions the total variation observed in the data (as measured by the sum of squares of deviations about the mean) into components which are attributable to each variable. An F-ratio is calculated as the ratio of the mean square of the variables to the mean square error term. As this F-ratio becomes progressively larger, the statistical significance of the variable becomes greater. Ordinarily a significance level in the range of five percent or less, which is associated with at least a 95 percent confidence level, is established as the criterion which must be met before it is concluded that there is a statistically significant effect.

More detailed discussions of the statistical designs and analysis of variance procedure used in the experiments are presented in Appendix D of this report.

The following sections present for each of the experiments, the statistical design features, the sampling system operating parameters, sample weights and final test results, and the statistical analysis of the test data. Tables which give the stack conditions and the sampling system operational data for each tests are presented in Appendices B and C, respectively.

Anisokinetic Sampling Experiments

Sixteen tests were performed to investigate the magnitude of anisokinetic sampling effects on the particulate collection process. The statistical pattern for the tests is given in Table 5. This pattern was derived from the use of confounded factorial experimental design which permitted the investigation of effects due to anisokinetic sampling, sampling systems, and any interaction effect between anisokinetic sampling and sampling system. Replication of each pair of test conditions was performed to increase the power of the statistical tests for detecting significant differences due to anisokinetic sampling. In performance of the test series, operators were randomly assigned to the control modules to minimize any bias due to sampling system operation.

Sampling was performed to compare results obtained at isokinetic rates and the following anisokinetic conditions:

1. 0.7 times isokinetic rate
2. 1.3 times isokinetic rate.

These anisokinetic conditions, outside the acceptable range for Method 5 results, were selected to accentuate any observable effects on particulate collections.

The results of the anisokinetic sampling experiments are presented in Table 6. The table gives the filter and probe sample weights and the particulate concentrations reported in mg/Nm^3. Analysis of the probe residues from all tests showed that variable quantities of ammonium sulfate and/or ammonium bisulfate were formed in the probe when the temperature was that specified in Method 5, i.e., 121 C (250 F) at the probe outlet (neither ammonium sulfate nor ammonium bisulfate were not detected in the filter catch). Consequently, any effects resulting from anisokinetic sampling were inadvertently confounded with mass variations due to ammonium sulfate formation. In order to resolve the test data, the following procedure was used to correct for the extraneous ammonium sulfate in each probe residue.

TABLE 9. RANDOMIZED TEST DESIGN FOR ANISOKINETIC SAMPLING STUDY

Test No.	Statistical Design Block No.	SYSTEM A Isokinetic Condition, %	SYSTEM B Isokinetic Condition, %
1	16	100	70
2	14	100	100
3	15	70	100
4	3	100	130
5	12	100	70
6	1	100	100
7	6	130	130
8	9	70	70
9	13	70	70
10	2	130	130
11	7	130	130
12	4	130	100
13	5	100	100
14	8	130	100
15	10	100	100
16	11	70	100

The corrections were made from the ratio of calcium in the probe and filter catches and the filter catch by using the equation:

$$PW\ (corrected) = \left[\frac{Ca\ (probe)}{Ca\ (filter)}\right] \left[FW\right]$$

where

PW (corrected) = probe residue weight corrected for ammonium sulfate

FW = weight of filter catch

Ca(probe) = weight of calcium in probe residue

Ca(filter) = weight of calcium in filter catch.

This approach assumes that calcium, the most abundant element in the particulate emissions, is present in the same weight percentage in both the filter and probe catches. Chemical analysis data presented a following section corroborate that this is a reasonable assumption.

The differences between the actual and corrected probe weights provide a measure of the quantity of ammonium sulfate formed which in the extreme cases accounts for almost 90 percent of the probe residue weight.

The particulate concentrations, which were used in the statistical analysis, were calculated from the corrected probe residue weight data.

Table 7 and 8 present the particulate emission data in the confounded factorial design format. The statistical design blocks numbered one to eight were used to compare the results obtained at isokinetic and hyperisokinetic conditions. The remaining statistical design blocks numbered nine through sixteen were used to compare the results obtained at isokinetic and subisokinetic conditions.

In Tables 7 and 8, the data from Blocks 1, 2, 5 and 6 and Blocks 3, 10, 13 and 14 have effects of isokinetic sampling conditions confounded with blocks (i.e., with source variations over time), and were used to measure the effects of systems and the interaction effect of systems with isokinetic sampling

TABLE 6. SAMPLE WEIGHT DATA-ANISOKINETIC SAMPLING EXPERIMENTS

Run No.	Nominal Percent Isokinetic	Sample Weights, mg				
		Filter	Probe (actual)	Probe (Corrected)	Total	mg/m^3
1A	100	41.8	47.2	9.4	51.2	22.8
B	70	30.7	43.1	9.7	40.4	25.4
2A	100	61.3	44.3	11.5	72.8	31.4
B	100	64.4	14.9	7.9	72.3	31.6
3A	70	51.7	34.0	16.2	67.9	43.1
B	100	71.2	44.2	18.4	89.6	61.8
4A	100	55.2	28.3	9.3	64.5	30.4
B	130	71.7	17.8	9.8	81.5	38.9
5A	100	58.9	42.1	11.5	70.4	32.2
B	70	42.0	16.2	7.4	49.4	31.9
6A	100	59.3	39.3	15.9	75.2	34.7
B	100	58.7	36.0	13.7	72.4	33.2
7A	130	70.7	20.4	9.4	80.1	38.7
B	130	68.5	13.0	7.2	75.7	36.8
8A	70	29.0	20.7	10.5	39.5	26.1
B	70	29.6	10.4	7.0	36.6	23.7
9/	70	30.5	12.5	10.3	40.8	27.2
B	70	30.2	7.7	5.0	35.2	22.4
10A	130	75.1	18.0	13.7	98.8	32.9
B	130	80.2	11.7	7.1	87.3	31.2
11A	100	54.7	63.7	9.7	64.4	30.2
B	130	67.3	11.9	8.2	75.3	27.4
12A	130	94.6	23.0	14.7	109.3	38.8
B	100	69.5	17.4	14.3	83.8	38.3
13A	100	64.7	46.8	12.0	76.7	34.9
B	100	64.5	47.1	11.7	76.2	33.7
14A	130	123.1	61.1	62.0	184.2	64.7
B	100	110.7	83.8	61.2	171.9	81.9
15A	100	71.3	60.5	34.8	106.0	49.1
B	100	72.8	79.0	16.5	89.3	41.3
16A	70	48.4	62.5	17.5	65.9	42.8
B	100	66.7	85.2	18.0	84.7	38.3

TABLE 7. STATISTICAL ANALYSIS DATA - ANISOKINETIC SAMPLING STUDY
ISOKINETIC VERSUS HYPERISOKINETIC CONDITIONS

(Measurements are in mg/Nm^3)

Sampling Condition	System	Replication / Block	1				2			
			1	2	3	4	5	6	7	8
Isokinetic	A		34,7	--	30,6	--	34,9	--	30,2	--
	B		33,2	--	--	38,3	33,7	--	--	81,9
1,3 S Isokinetic	A		--	32,8	--	36,6	--	28,7	--	64,7
	B		--	31,3	28,9	--	--	26,8	27,4	--

Blocks 1, 2, 5, 6 are confounded with isokinetic conditions effect
Blocks 3, 4, 7, 8 are confounded with isokinetic conditions x systems interaction effect

TABLE 8. STATISTICAL ANALYSIS DATA ANISOKINETIC SAMPLING STUDY
ISOKINETIC VERSUS SUBISOKINETIC CONDITIONS

(Measurements are in mg/Nm^3)

Sampling Condition	System	Replication / Block	1				2			
			9	10	11	12	13	14	15	16
Isokinetic	A		--	40,1	--	38,3	--	31,4	--	33,8
	B			41,2	38,3	--	--	31,6	41,8	--
0,7 S Isokinetic	A		26,1	--	42,8	--	37,8	--	43,1	--
	B		33,7	--	--	31,9	33,4	--	--	83,4

Blocks 1, 2, 5, 6 are confounded with isokinetic conditions effect
Blocks 3, 4, 7, 8 are confounded with isokinetic conditions x systems interaction effect.

conditions. Blocks 3, 4, 7, and 8 in Table 7 and Blocks 11, 12, 15, and 16 in Table 8 do not have isokinetic sampling conditions confounded and are suitable for estimating the magnitude of the effects due to hyperisokinetic and subisokinetic sampling conditions.

In Tables 9 and 10, the statistical significance of these differences are tested. The statistical test used is an accepted analysis of variance procedure. In Table 9, comparing isokinetic and hyperisokinetic sampling conditions data, the F-ratio of 2.74 is associated with an 84 percent confidence level, or a 16 percent significance level. In Table 10, the F-ratio of 1.34 determined from analysis of the isokinetic conditions is associated with a 70 percent confidence level, or a 30 percent significance level. In neither case is the usual criterion for statistical significance met i.e. a 95 percent confidence level or a 5 percent significance level. Consequently, the conclusions drawn from Tables 9 and 10, are that variations in particulate collections due to anisokinetic sampling, or to interaction effects of systems and conditions are not significant based on the normal criteria i.e. significance at the 95 or 99 percent confidence level.

TABLE 9. ANALYSES OF VARIANCE-ANISOKINETIC SAMPLING EXPERIMENT (ISOKINETIC VERSUS HYPERISOKINETIC CONDITIONS)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Ratio	Conclusion
Systems(S)	2.40	1	2.40	0.12	Not Significant
Isokinetic Conditions (C)	55.12	1	55.12	2.76	Not Significant
CxS Interaction	0.08	1	0.08	0.01	Not Significant
Replications	223.50	1	223.50	--	
Blocks Within Replications	2910.10	6	485.02	--	
Error (Remainder)	100.41	5	20.08	--	
Total	3291.63	15	--	--	

TABLE 10. ANALYSES OF VARIANCE-ANISOKINETIC SAMPLING EXPERIMENT ISOKINETIC CONDITIONS VERSUS SUBISOKINETIC CONDITIONS

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Ratio	Conclusion
Systems(S)	21.16	1	21.16	3.45	Not Significant
Isokinetic Conditions(C)	8.20	1	8.20	1.34	Not Significant
CxS Interaction	0.03	1	0.03	0.01	Not Significant
Replications	98.01	1	98.01	--	
Blocks Within Replications	919.71	6	153.28	--	
Error (Remainder)	30.63	5	6.13	--	
Total	1077.74	15	--		

Filter Size, Temperature, and Nozzle Configuration Experiments

Three experimental factors were varied in this test series, each at two levels:

(1) Filter size: 6.4mm (2.5 in.) versus 10.2cm (4 in.)

(2) Temperature: Stack ~ 205 C versus 121 C; and

(3) Nozzle type: Goose neck nozzle versus 90° nozzle.

With two levels for each of the three factors, eight combinations of experimental conditions were possible. Since only two ports were suitable for sampling, only two of these combinations could be run simultaneously. Thus it was necessary to use an experimental design which would selectively confound information on some of the effects with the variation which might be expected from varying stack conditions over time. The design used for this experiment was the partially confounded factorial design. Each combination of the three factors was performed three times. The combinations were assigned to simultaneous pairs (statistical blocks) in such a way that varying stack conditions over time would be confounded in a balanced manner allowing partial information on the effects of each of the three factors being studied as well as information on the effects of first order interaction of these factors (i.e., their effects in combination which may be more than the sum of their individual effects). The statistical blocks were randomly ordered over time and the two Method 5 trains were randomly assigned within each block. The randomized test pattern used for the experiment is shown in Table 11. Operators were also randomly assigned to sampling systems.

The data collected for this experiment are shown in Table 12. In Table 13, the data are shown in the format of the confounded factorial design. The statistical analyses of these data are present in Table 14. With the same criterion as before, the F-ratios in the analysis of variance indicate that there is a significant difference in sample weights which is due to sampling system temperature. The confidence level associated with this F-ratio of 39.36 is greater than 99 percent. A significant effect due to filter size is also noted. The F-ratio of 5.37, indicates at a confidence level of approximately 94 percent, that differences between filters are significant. The effect of nozzle configuration, or of any interaction effects are not statistically significant.

Further examination of the significant factors are presented in Table 15.

TABLE II. RANDOMIZED TEST PATTERN FOR STUDY OF FILTER SIZE, TEMPERATURE, AND NOZZLE CONFIGURATION

Order of Test	System A[a]			System B[a]			Block No. in Statistical Design
	Filter Size, cm	Temp, C	Type Nozzle[b]	Filter Size, cm	Temp, C	Type Nozzle	
1	10.2	Stack[c]	G	6.4	Stack	90°	8
2	6.4	121	G	6.4	Stack	90°	1
3	6.4	Stack	90°	10.2	121	90°	12
4	6.4	Stack	G	10.2	Stack	90°	7
5	10.2	121	90°	6.4	121	G	5
6	10.2	Stack	90°	10.2	121	G	2
7	10.2	121	G	6.4	Stack	G	10
8	6.4	Stack	G	6.4	121	90°	3
9	10.2	121	G	6.4	121	90°	6
10	10.2	Stack	90°	6.4	121	90°	11
11	6.4	121	G	10.2	Stack	G	9
12	10.2	121	90°	10.2	Stack	G	4

(a) Systems A and B are both Method 5 trains with variations as shown.
(b) G = goose neck nozzle, 90°=90° nozzle.
(c) Stack temperature was about 205C.

TABLE 12. SAMPLE WEIGHT DATA-FILTER SIZE, TEMPERATURE, AND NOZZLE CONFIGURATION STUDY

Run No.	Nominal Test Conditions: Filter Diam, cm	Temperature, C	Nozzle[a]	Sample Weights, mg: Filter	Probe	Total	mg/Nm³
17A	10.2 (4in.)	Stack[b]	G	51.9	9.9	61.8	27.2
B	6.4 (2.5in.)	Stack	S	42.8	14.3	57.1	24.7
18A	6.4	121(250 F)	G	67.1	39.5	106.6	46.1
B	6.4	Stack	S	74.7	12.9	87.6	37.9
19A	6.4	Stack	S	59.0	12.2	71.2	34.6
B	10.2	121	S	50.8	40.3	91.1	44.3
21A	6.4	Stack	G	60.1	9.3	69.4	40.1
B	10.2	Stack	S	61.3	10.0	71.3	30.9
22A	10.2	121	S	53.9	26.3	80.2	34.2
B	6.4	121	G	50.7	22.9	73.6	31.1
23A	10.2	Stack	S	36.9	4.5	41.4	17.3
B	10.2	121	G	28.2	16.7	44.9	18.4
24A	10.2	121	G	34.5	19.5	54.0	24.6
B	6.4	Stack	G	23.7	6.1	29.8	13.0
25A	6.4	Stack	G	36.9	14.5	51.4	22.1
B	6.4	121	S	31.9	25.5	57.4	24.3
27A	10.2	121	G	43.8	31.4	75.2	34.7
B	6.4	121	S	39.3	25.4	64.7	29.9
28A	10.2	Stack	S	63.1	15.1	78.7	34.8
B	6.4	121	S	49.7	43.4	93.1	41.5
29A	6.4	121	G	40.2	24.4	64.6	28.4
B	10.2	Stack	G	46.4	9.2	55.6	24.2
31A	10.2	121	S	80.8	32.6	93.4	40.3
B	10.2	Stack	G	69.7	10.4	80.1	33.9

(a) G - Goose neck nozzle, S - 90° nozzle.

(b) Stack temperature was about 205C.

TABLE 13. DATA USED IN STATISTICAL ANALYSIS OF FILTER SIZE, TEMPERATURE, & NOZZLE CONFIGURATION EFFECTS

(Measurements are in mg/Nm^3)

Filter Size, F		5.6 cm		10.2 cm	
Temperature, T		121 C	Black	121 C	Black
Nozzle	Goose Neck	(1) 46.1	(3) 22.1	(2) 18.4	(4) 33.9
		(5) 31.1	(7) 30.1	(6) 34.7	(8) 27.2
		(9) 28.6	(10) 13.0	(12) 24.6	(9) 24.2
	90° Nozzle	(3) 24.3	(1) 37.3	(4) 40.3	(2) 17.3
		(6) 29.9	(8) 24.7	(5) 34.2	(7) 30.9
		(11) 41.5	(12) 34.6	(12) 44.3	(11) 34.8

Numbers in parentheses, indicate statistical block number.

Rep 1, Blocks 1, 2, 3, 4 are confounded with mean effect, F, and interaction effects, TN and FTN.
Rep 2, Blocks 5, 6, 7, 8 are confounded with mean effect, T, and interaction effects, FN and FTN.
Rep 3, Blocks 9, 10, 11, 12 are confounded with mean effect, N, and interaction effects, FT and FTN.

TABLE 14. ANALYSIS OF VARIANCE FILTER SIZE, TEMPERATURE, AND NITRIC CONCENTRATION STUDY

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F(a) Ratio	Information from Blocks	Conclusion
F, Filter Size	1	29.16	29.16	5.37	5,6,7,8,9,10,11	Significant at the 95% Confidence Level
T, Temperature	1	159.39	159.39	29.36	1,2,3,4,9,10,11, 12	Significant at the 99% Confidence Level
N, Nitric	1	1.27	1.27	0.23	1,2,3,4,5,6,7,8	Not Significant
FT	1	0.11	0.11	0.02	1,2,3,4,5,6,7,8	Not Significant
FN	1	3.33	3.33	0.61	1,2,3,4,9,10,11, 12	Not Significant
TN	1	0.02	0.02	0.01	5,6,7,8,9,10,11 12	Not Significant
FTN	-	-	-	-	None	
Reps	2	1.86	0.93	-	All	
Blocks Within Reps	9	1438.84	159.87	-	All	
Remainder	6	32.57	5.43	-	All	
Total	23	1637.78			All	

(a) For an F-ratio with 1 and 6 degrees of freedom, as in this table, any calculated value of F exceeding 3.78 is significant at the 90 percent confidence level, exceeding 5.99 is significant at the 95 percent confidence level, or exceeding 13.78 is significant at the 99 percent confidence level.

TABLE 15. COMPARISON OF LEVEL OF SIGNIFICANT FACTORS - FILTER SIZE, TEMPERATURE, AND NOZZLE CONFIGURATION STUDY

Factor	Level 1		Level 2		Difference in Mean Effect (Level 1 - Level 2)	Percentage Difference
	Description	Mean Effect[a]	Description	Mean Effect[a]		
Filter Size	6.4	29.2 mg/Nm^3	10.2	31.9 mg/Nm^3	-2.7 mg/Nm^3	-8.5
Temperature	121	33.5 mg/Nm^3	Stack	27.2 mg/Nm^3	+6.3 mg/Nm^3	+23.2

(a) Using only data from those statistical blocks identified in Table 14.

The effect of using the smaller 5.4cm filter is a 9.3 percent decrease the in average sample weight collected as compared with the 10.2cm filter. This difference was shown to be statistically significant at the 95 percent confidence level. The most statistically significant result is due to sampling system temperature. Operation of the Method 5 train at the normal probe and filter box temperatures yield particulate results with average sample weights which are 23.2 percent higher than results obtained when the sampling system temperature is maintained at about 205C. This result is significant at a confidence level of greater than 99 percent.

In summary, the results indicate that significant particulate mass differences resulted from variation of the filter size and the sampling system temperature. Significant differences due to nozzle configuration or to any interaction of the three factors, filter size, temperature, and nozzle design were not observed.

Filter Box/Probe Temperature Experiments

Three combinations of probe and filter temperatures were studied in this experiment:

(1) Both at stack temperature (~205 C),

(2) Both at 121~C; and

(3) Probe at stack (205 C), filter box at 121 C.

Since only two temperature combinations could be run concurrently, three separate collection runs were necessary so that every possible pair of temperature combinations could be operated simultaneously. Each of these pairs was repeated three times to increase the power of the statistical analysis. The randomized experimental design for these nine statistical blocks is shown in Table16. The temperature combinations and operators were randomly assigned to the two sampling systems.

Table 17 summarizes the data collected for this experiment. In Table 18, data are given in the incomplete randomized block pattern in which the experiment was performed. The adjusted treatment means shown at the bottom of Table 18 have the effect of varying stack conditions removed by the standard statistical procedure described in Appendix D. Comparisons among these adjusted treatment means represent the best estimate of the differences in the sampling methods due to the temperature operating conditions of the filter box and probe.

Table 19 presents the statistical analysis of the test data. The F-ratio, 6.77 indicates, at the 98 percent confidence level, that there is a statistically significant difference in results obtained with the three sampling system temperature operating conditions.

The significance of differences between the various pairs of sampling temperature conditions can be evaluated by examination of the adjusted treatment means given in Table 18. The adjustment is necessary to avoid contaminating differences in means with temporal variations in the source emissions. Significances at confidence levels of 95 and 99 percent are associated with adjusted mean differences of 7.49 and 11.09 mg/Nm^3, respectively. The method of determining these critical values is described in Appendix D. Thus, the respective differences of 10.0 and 10.1 mg/Nm^3, (about 43 percent difference) indicate with greater than 95 percent confidence that results obtained with both

TABLE IX. RANDOMIZED EXPERIMENTAL DESIGN TO STUDY THE EFFECT OF PROBE AND FILTER TEMPERATURE COMBINATIONS

Test No.	Statistical[a] Block No.	System A Temperatures, C		System B Temperatures, C	
		Probe Outlet	Filter Box	Probe Outlet	Filter Box
1	1	121	121	Stack	Stack
2	8	121	121	Stack	121
3	4	Stack	Stack	121	121
4	9	Stack	Stack	Stack	121
5	2	Stack	121	121	121
6	7	121	121	Stack	Stack
7	6	Stack	121	Stack	Stack
8	3	Stack	Stack	Stack	121
9	5	121	121	Stack	121

TABLE 17. SAMPLE WEIGHT DATA-FILTER BOX/PROBE TEMPERATURE EXPERIMENTS

Run No.	Nominal Temperatures, C		Sample Weights, mg			
	Filter Box	Probe	Filter	Probe	Total	ug/Nm³
32A	121 (250 F)	121	40.8	76.3	117.1	56.2
B	Stack (~400)	Stack	41.5	36.0	77.5	36.8
33A	121	121	39.7	80.7	120.4	58.5
B	121	Stack	38.7	41.2	79.9	38.5
34A	Stack	Stack	25.9	9.8	35.7	16.5
B	121	121	20.5	25.1	45.6	20.6
35A	Stack	Stack	32.7	11.7	44.4	21.4
B	121	Stack	30.0	11.7	41.7	20.1
36A	121	Stack	27.1	7.8	34.9	16.4
B	121	121	24.3	14.9	39.2	18.3
37A	121	121	36.1	23.4	51.5	23.4
B	Stack	Stack	29.6	8.1	37.7	17.3
38A	121	Stack	30.9	16.2	47.1	21.5
B	Stack	Stack	32.2	8.5	40.7	18.9
39A	Stack	Stack	30.4	14.1	44.5	20.1
B	121	Stack	28.2	13.4	41.6	19.1
40A	121	121	27.9	40.1	68.0	30.6
B	121	Stack	27.8	18.4	46.2	21.3

TABLE 18. DATA FOR STATISTICAL ANALYSIS -- FILTER BOX/PROBE TEMPERATURE EXPERIMENTS

(Results are in mg/Nm^3)

Statistical Block No.	Temperature Combinations		
	Probe: 121 C; Filter Box: 121 C (A)	Stack (~205 C) (B)	Stack (~205 C); 121 F (C)
1	36.2	36.8	--
2	18.3	--	16.4
3	--	20.1	19.1
4	20.4	16.5	--
5	30.6	--	21.3
6	--	18.9	21.5
7	23.4	17.3	--
8	36.5	--	38.3
9	--	21.4	20.1
Treatment Means Adjusted for Block Effects	33.1 mg/Nm^3	33.1 mg/Nm^3	23.0 mg/Nm^3

Differences in adjusted treatment means:

A-B = 10.0 mg/Nm^3
A-C = 10.1 mg/Nm^3
B-C = 0.1 mg/Nm^3

TABLE 19. ANALYSIS OF VARIANCE -- FILTER BOX/PROBE TEMPERATURE EXPERIMENT

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-ratio[a]	Conclusion
Between Filter Box/ Probe Temperatures Combinations	306.07	2	153.04	6.77	Significant at the 95% Confidence Level
Between actual Block Totals	2381.86	6	(discard)	--	
Remainder (Error Term)	158.10	7	22.59		
Total	2846.03	17			

(a) For an F-ratio with 2 and 7 degrees of freedom, as in this table, any calculated value of F exceeding 5.59 is significant at the 95 percent confidence level, or exceeding 9.55 is significant at the 99 percent confidence level.

the 205C probe/205C filter and 205C probe/121 C filter conditions are significantly lower than results obtained with the 121 C probe/121 C filter. Results obtained with the 205 C probe/205 C filter temperatures and with 205 C probe/121 C filter temperatures are not significantly different.

In-Stack Filter Experiments

Experiments were performed to compare particulate measurements made with the following three types of filters:

(1) In-stack flat filter,

(2) In-stack thimble filter, and

(3) Method 5 hot filter.

The probes and filter boxes were operated at about 205 C and 121 C, respectively, for tests with all three filter types.

Since only two filter types could be evaluated simultaneously in the stack, three separate collection runs were necessary in order to operate every possible pair of filter types concurrently. To increase the power of the statistical analysis, the use of each pair of filter types was repeated three times, resulting in nine statistical blocks of data collection. These nine statistical blocks were randomly ordered over time and filter types were randomly assigned within blocks as shown in Table 20. The two operators were also randomly assigned to sampling systems.

The data collected for this experiment are displayed in Table 21. These data fit the incomplete randomized block design as shown in Table 22. The adjusted treatment means shown have had the effects of varying stack conditions removed, and comparisons between these means reflect best estimates of the differences in the sample system due to the type of filter used. Data are given for nozzle and filter catch and for total system catch (nozzle, filter, probe, and backup filter) in the in-stack filter runs.

The analyses of variance of the test data is summarized in Table 23. Using the data based on the nozzle and in-stack filter collections, an F-Ratio of 12.78 obtained from this analysis. This F-ratio indicates that there are high significant differences in results obtained with the various types of filters.

The differences in adjusted treatment means shown in Table 22 can be examined to reveal significant differences in results obtained with the various filter types. An observed difference in adjusted treatment means which exceeds 3.7 mg/Nm^3 an observed difference which exceeds 3.5 mg/Nm^3 is statistically significant at the 99 percent confidence level. Therefore, the respective differences of 6.7 and 7.0 mg/Nm^3 between the in-stack thimble and the in-stack flat and the Method 5 results are statistically significant at a confidence levels greater than 99 percent. The difference of 0.3 mg/Nm^3 between the in-stack flat filter and Method 5 results is not statistically significant. These conclusions are based on only the nozzle and in-stack filter collections in the in-stack filter runs. Use of the total system collections for the in-stack filter experiments does not change these conclusions.

TABLE 8B. RANDOMIZED STATISTICAL DESIGN FOR COMPARISON OF PARTICULATE MEASUREMENTS WITH METHOD 5 AND TWO TYPES OF IN-STACK FILTERS

Test No.	Statistical Block No.	System A Filter Type	System B Filter Type
1	6	In-stack thimble	In-stack flat
2	3	In-stack flat	In-stack thimble
3	1	Method 5	In-stack flat
4	5	In-stack thimble	Method 5
5	4	In-stack flat	Method 5
6	8	In-stack thimble	Method 5
7	2	Method 5	In-stack thimble
8	9	In-stack flat	In-stack thimble
9	7	Method 5	In-stack flat

[illegible]

Item No.	Filter Type[a]	Cadmium Weight, mg					Cadmium Concentration[b]			Cadmium Distribution, Percent of Total Collected					
		Jar Rinse	In-Stack Filter	Probe	Nozzle	Total				Jar Rinse	In-Stack Filter	Probe	Nozzle	Filter & Nozzle	Initial Filter
41	Thimble	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	Filter	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
42	Filter	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	Thimble	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
43	Method 5	[illegible]	—	[illegible]	—	[illegible]	[illegible]			[illegible]	—	[illegible]	—	—	—
	Filter	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
44	Thimble	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	Method 5	[illegible]	—	[illegible]	—	[illegible]	[illegible]			[illegible]	—	[illegible]	—	—	—
45	Filter	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	Method 5	[illegible]	—	[illegible]	—	[illegible]	[illegible]			[illegible]	—	[illegible]	—	—	—
46	Thimble	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	Method 5	[illegible]	—	[illegible]	—	[illegible]	[illegible]			[illegible]	—	[illegible]	—	—	—
47	Method 5	[illegible]	—	[illegible]	—	[illegible]	[illegible]			[illegible]	—	[illegible]	—	—	—
	Thimble	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
48	Filter	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	Thimble	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
49	Method 5	[illegible]	—	[illegible]	—	[illegible]	[illegible]			[illegible]	—	[illegible]	—	—	—
	Filter	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

(a) [illegible]

(b) [illegible]

TABLE 22. DATA FOR STATISTICAL ANALYSIS -- IN-STACK FILTER EXPERIMENTS(a)

Statistical Block No.	Filter Type: In-stack thimble (A)		In-stack Flat (B)		Method 5 (C)
1	--		36.9	(38.3)	36.1
2	34.9	(36.3)	--		26.9
3	48.5	(51.1)	40.1	(42.4)	--
4	--		35.7	(37.9)	37.4
5	36.8	(38.6)	--		46.6
6	37.1	(39.1)	36.9	(38.3)	--
7	--		33.3	(36.1)	38.7
8	31.6	(33.6)	--		23.1
9	48.7	(50.9)	42.9	(45.6)	--
Treatment Means Adjusted for Block Effect	45.4 mg/H_m^3 (47.3)		38.7 mg/H_m^3 (40.7)		38.4 mg/H_m^3

Difference in adjusted treatment means:

A-B = 6.7 (6.6) mg/Hm^3
A-C = 7.0 (8.9) mg/Hm^3
B-C = 0.3 (2.3) mg/Hm^3

(a) Analysis based on nozzle and filter catch. Values in parenthesis are calculated from total system catch.

TABLE 23. ANALYSIS OF VARIANCE -- IN-STACK FILTER EXPERIMENTS[a]

Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	F-ratio[b]	Conclusion of Statistical Test
Between Corrected Treatment (Filter-types) totals	141.13 (193.64)	2	70.57 (16.82)	12.78 (20.87)	Significant at the 99% Confidence Level
Between actual Block totals	1496.81 (1382.81)	8	(discard)	--	
Remainder (Error term)	38.68 (32.49)	7	5.52 (4.64)	--	
Total	1676.62 (1808.94)	17			

(a) Analysis based on nozzle and filter catch. Values in parenthesis are based total system catch.

(b) For an F-ratio with 2 and 7 degrees of freedom, as in this table, any calculated value of F exceeding 5.59 is statistically significant at the 95 percent confidence level, or exceeding 9.55 is statistically significant at the 99 percent confidence level.

In summary, the results using only the nozzle and filter catch in in-stack filter experiments indicate that the use of the in-stack thimble filter yields particulate concentrations which are 17 and 18 percent higher than the respective in-stack flat and Method 5 filter results. Respective differences based on total catch of the in-stack systems are 16 and 23 percent. Statistically comparable results were obtained by Method 5 and in-stack flat filter sampling.

Characterization of Kiln Emissions and Particulate Collections

General Chemical Composition of Particulates

Extensive chemical analyses were performed on a grab sample and filter and probe samples obtained in the earlier sampling effort[5]. The results of the analyses are summarized in Table 24. Within the limits of sampling and analytical error, the composition of collections with the Method 5 sampling system appear the same as the grab sample, which should be representive of the particulate emissions.

Analyses of particulate samples obtained during concurrent sampling with Method 5 (206 C probe and 129 C filter box) and an in-stack flat filter system are presented in Table 25. The particulate samples were removed from the filter medium before analysis. The probe and nozzle samples were residues from an acetone rinse of these components. With the exception of Na and K, there appear to be no significant differences in the elemental composition of the samples. Sodium and potassium concentrations in the filters are significantly higher than concentrations in the Method 5 probe and in-stack system nozzle samples. However, total Na and K in samples collected with the two types of trains is approximately the same.

Selected Chemical Analysis of Particulate Collections

A white crystalline material was found, in varying quantities, in all Method 5 probe residue samples when sampling was performed using filter box and probe outlet gas temperatures of 121 C (250 F). A pair of probe residue samples (Runs 15A and 8) containing the material are shown in Figure 16.

Infrared spectrometry (IR), X-ray diffraction (XRD), and classical chemical analysis were employed to identify the extraneous material in the probe collections. Results from these analyses confirmed that the substance was ammonium sulfate, $(NH_4)_2SO_4$.

The IR spectrum of a probe residue sample is shown in Figure 17. A reference spectrum of ammonium sulfate obtained under the same conditions (KBr pellet) is presented for comparison. The ammonium ion is indicated by the spectral structure centering near 3150 cm^{-1} (N-H stretch) and by absorption at 1400 cm^{-1} (N-H deformation). The asymetric stretching frequency of the sulfate absorbs at 1100 cm^{-1}. The band a 613 cm^{-1} is also indicative of sulfate structure. Weak bands near 650 cm^{-1} may indicate the presence of small amounts of other sulfates.

TABLE 7-4. ANALYSES OF GRAB SAMPLE AND METHOD 5 PARTICULATE SAMPLES

Sample	Composition, weight percent													
	Al	C	Ca	Cl	Fe	H	K	Mg	N	Na	S	Si	CO_3	SO_4
Grab Sample	2.7	7.2	26.2	0.4	1.3	0.3	3.5	0.7	0.1	0.5	1.2	5.3	36.6	3.4
Method 5 (Average)														
Filter catch	1-5		28-48		1-5		1-5	.5-2		1-5		5-10	17-46	6-15
Probe catch	3-10		28-50		1-10		5-20	1-5		1-10		3-10		7-15

TABLE 35. ANALYSIS OF PARTICULATE COLLECTIONS FROM METHOD 5 AND IN-STACK SAMPLING

Sample	Elemental Composition, weight percent[a]																	
	Al	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Si	Sn	Sr	Ti	V	Zn
Method 5[b]																		
Filter catch	1.	.03	15-25	<.01	.005	1.	15-25	1.	.1	5.	<.01	.04	5.	<.01	.04	.3	.01	<.1
Probe catch	1.	.02	10-15	.02	.03	1.	2.	1.	.05	.5	.01	.02	5.	.05	.02	.1	<.01	.2
In-Stack Flat Filter[b]																		
Filter catch	1.	.02	15-25	<.01	.005	2.	15-25	.8	.1	4.	<.01	.04	5.	<.01	.04	.3	.01	<.1
Nozzle catch	2.	.01	10-15	.07	.02	1.	1.	.5	.1	1.	.05	.02	5.	.03	.02	.1	<.01	.5

(a) Analyzed by optical emission spectroscopy
(b) Samples from Run No. 438
(c) Samples from Run No. 439

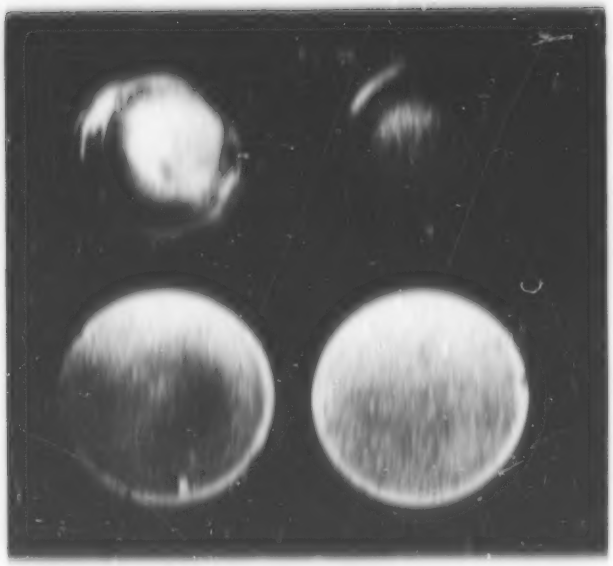


FIGURE 16. PROBE RESIDUES SHOWING CRYSTALLINE MATERIAL OBTAINED FROM SAMPLING WITH METHOD 5

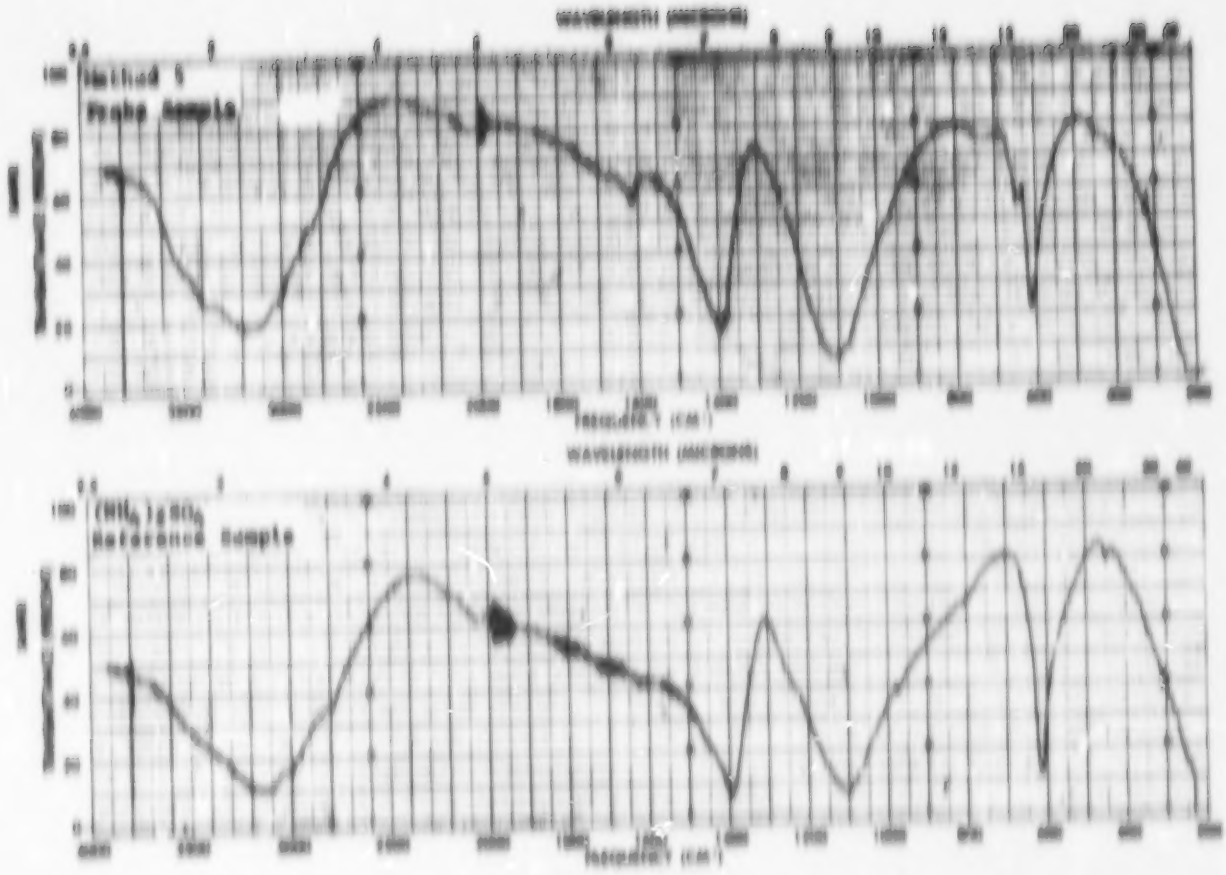


FIGURE 17. INFRARED SPECTRA OF PROBE RESIDUE AND AMMONIUM SULFATE REFERENCE SAMPLE

A trace of an organic carbonylic acid salt could be indicated by absorption at 1620 cm^{-1} and the very weak shoulders at 2920 and 2840 cm^{-1}.

XRD patterns were obtained by placing a small amount of the probe residue on a glass fiber and exposing the sample to FeKα x-rays in a 57.3 mm diameter Debye-Scherrer Camera. The pattern obtained matched that for Mascagnite $(NH_4)_2SO_4$. (Powder Diffraction File Number 10-343). The following lines attributable to ammonium hydrogen sulfates were not present in the sample pattern:

NH_4HSO_4	4.75 and 3.69 A
$(NH_4)_3H(SO_4)_2$	4.93, 4.98 and 3.77 A

The following lines were present in the sample pattern were not identified:

Line, A	Intensity
5.69	Weak
3.55	Very weak
2.87	Very weak
2.734	Weak
2.553	Very, very weak
2.242	Very, very weak

Classical chemical analysis for NH_4 and SO_4 in the crystalline probe material were performed by Kjeldahl and barium perchlorate-thorin titration procedures, respectively. The results confirm the presence of NH_4 and SO_4 in a ratio consistent with the stoichiometry of $(NH_4)_2SO_4$.

Potential interactions during sampling include condensation of ammonium sulfates and/or sulfuric acid and reaction of sulfur oxides with the filtermedium and/or collected particulates. Accordingly, selected samples were analysed for NH_4^+ and $SO_4^=$ ions to investigate the formation of extraneous sulfate during the sampling process. Calcium was also determined to provide a relative measure of cementitious material in the samples.

Analyses of filter samples were performed by digestion of the filter and particulate catch in hot, dilute hydrochloric acid. Ammonium determinations were performed by the Kjeldahl method; sulfate by barium perchlorate -- thorin titration; and, calcium by atomic absorption spectrometry. Corrections were applied for background (blank) levels of Ca, NH_4^+, and $SO_4^=$ found in unused filters.

The data in Table 26 were obtained from analyses of filter and probe samples collected with various probe and filter box operating temperatures. Filter analysis was performed by digestion of sample and the filter medium. Corrections were applied for filter blanks.

TABLE 26. ANALYSES OF FILTER AND PROBE SAMPLES FROM EXPERIMENTS USING VARIOUS FILTER/PROBE TEMPERATURE COMBINATIONS

Run No.	Operating Temperature, °C			Filter Catch mg	Weight Percent in Filter Catch			Probe Catch mg	Weight Percent in Probe Catch			Ratio Probe NO_x/SO_x
	Probe	Outlet	Filter Box		Cr	NO_x	SO_x		Cr	NO_x	SO_x	
34A	288	285	25.9	17.1	<LA	23.9	9.8	16.6	<1	7.1	—	
B	124	122	28.5	18.6	<LA	25.4	25.1	9.6	6.4	29.5	.22	
35A	148	123	27.1	14.5	<LA	28.4	7.8	17.9	<1	38.3	—	
B	122	125	24.3	14.7	<LA	29.2	14.9	12.8	4.7	29.5	.16	
37A	122	126	—	—	—	—	23.4	6.8	5.8	28.6	.21	
B	189	194					8.1	14.8	<1	21.8	—	
39A	188	123	—	—	—	—	16.2	16.8	<1	8.8	—	
B	189	203					8.5	13.4	<1	18.6	—	
39A	201	196					14.2	19.1	<1	7.8	—	
	188	123	—	—	—	—	13.4	19.8	<1	11.2	—	
40A	126	123	27.9	18.4	<LA	27.2	48.1	8.9	9.5	36.7	.26	
B	192	123	27.8	16.9	<LA	24.8	18.4	19.6	<1	8.2	—	

The high NH_4^+ and $SO_4^=$ concentrations in the probe samples from Runs 34B, 36B, 37A, and 40A indicate the formation of ammonium sulfates when the probe is maintained at about 121 C. The stoichiometric ratios of NH_4^+ and $SO_4^=$ suggest that bisulfate or mixtures of bisulfate and sulfate are formed. Ammonium sulfates were not detected in the filter catch when the lower probe temperature of 121 C (250F) was used.

The probe and filter samples obtained with a probe temperature of about 200 C and filter box temperature of either 121 C or 200 C do not show the formation of ammonium sulfates. These samples, however, show significantly higher percentages of sulfate in the filter analyses than in the probe analyses.

Analytical results of particulate samples from the Method 5 and in-stack filter comparison test are presented in Table 27. In concurrent tests, Method 5 and in-stack flat filter sampling gave similar results while the in-stack thimble yielded higher particulate mass results. The data in Table 27 show that calcium-to-sulfate ratios are the same for the Method 5 and in-stack flat filter catches. However, ratios are much lower for the in-stack thimbles due to much higher quantities of sulfate. If the weight of the thimble catch is corrected for "excess sulfate" by using the Ca/SO_4 ratio of the Method 5 or in-stack flat filter catch obtained concurrently, the results of the three configurations are in good agreement. The results indicate that the difference between the results obtained with the in-stack thimble and Method 5 and the in-stack flat filter can be attributed to extraneous sulfate formation on the thimble.

The backup filters used behind the in-stack filters show generally lower quantities of Ca and NH_4^+ and higher levels of sulfate which may indicate a reaction with sulfur oxides. However, the very low sample weights preclude any firm conclusions regarding these results. As noted in the previous data, the sulfate concentration in Method 5 filters is significantly higher than the probe sulfate content.

The high filter-to-probe ratio of sulfate (coupled with approximately equal Ca concentrations) suggest that extraneous sulfate may also be formed by reaction of sulfur oxides with the MSA 1106 BH filter medium. In order to investigate this possibility, filters from selected runs were halved (<5 mg difference in halves) and sulfate analyses were performed on one-half (filter and particulate) and on particulate samples (about 30 percent) catch carefully removed from the other half. The results showing distribution of the sulfate between the particulates and the filter (by difference) are given in Table 28. The results indicate that sulfur oxides also react to a lesser extent with MSA 1106 BH filter material when used in either Method 5 train or in-stack.

TABLE 27. CHEMICAL ANALYSES OF SAMPLES COLLECTED IN VARIOUS METHOD 5 AND IN-STACK SAMPLING TRAIN COMPONENTS

Run No.	Sample	Weight of Catch, mg	Particulate Composition, Weight Percent Ca	NH_4^+	SO_4
42A	In-stack flat filter	86.8	18.2	0.02	26.5
	Backup filter	3.3	2.2	1.3	41.7
42B	In-stack thimble	107.8	12.3	0.02	39.8
	Backup filter	3.9	2.6	0.8	23.0
43A	In-stack flat filter	77.7	16.0	0.03	39.3
	Backup filter	3.8	3.2	0.8	50.0
	Nozzle	4.9	10.8	<0.4	6.1
43B	Method 5 filter	76.3	16.3	<0.02	30.1
	Probe	14.0	17.6	<0.1	6.4
47A	Method 5 filter	57.4	18.8	<0.03	20.9
	Probe	10.5	13.6	<0.3	5.7
47B	In-stack thimble	79.0	12.8	<0.02	32.0

TABLE 28. SULFATE IN FILTERS AND PARTICULATE COLLECTIONS

Run No.	Filter[a] Configuration	Weight of Filter Catch, mg	Distribution of Sulfate, mg			Filter Sulfate Contribution, Percent
			Filter and Catch	Catch	Filter (difference)	
42A	In-stack Cint	90.6	14.1	6.1	8.0	8.8
44A	Method 5	106.7	32.6	16.9	16.7	15.7
48A	In-stack Cint	106.4	31.9	17.2	14.7	10.1
50A	Method 5	108.8	34.9	17.2	17.7	16.4

(a) Filter sizes: Method 5 - 8.3 cm (diameter) In-stack - 6.4 cm

inaccuracies in division of the filters would produce errors in the exact distributions, but the consistency of the results tends to verify that some sulfate is formed on the MFA filter. Assuming the data in Table 28 is reasonably accurate, the extraneous sulfate formation in the filter medium could produce significant errors, in this case about 16 percent.

In summary, the chemical analyses of samples obtained in this study support the following observations.

(1) The gross composition of cementitious particulate collections do not appear to be altered by the Method 5 sampling procedure

(2) Sampling with Method 5 as currently promulgated results in in formation of ammonium sulfates in the probe

(3) Precipitation of ammonium sulfates in Method 5 sampling can be eliminated by operation of the probe at about 205 C.

(4) Sulfur oxides, presumably sulfuric acid vapor, react with the Hunktell in-stack filter thimble.

(5) Reaction of sulfur oxides with MFA 1100 BH filter material is also indicated.

Impinger Analysis

The impinger samples from four pairs of tests in which sampling was performed with Method 5 trains were analyzed as described in the Federal Register, August 31, 1971. The results are presented in Table 39. Ammonium and sulfate analyses of the samples from Runs 23A and 23B show that ammonium sulfate accounts for 91 and 95 percent, respectively, of the water residue weight.

Particle Size Measurements

Particle size determinations were performed to characterize the particulate emissions from the cement kiln (after precipitator) and to aid in interpretation of the anisokinetic sampling data. Aerodynamic sizing was attempted with an Andersen in-stack impactor, but questionable results were obtained. A large fraction (about 40 percent) of the total catch was deposited on the impactor wall prior to the first stage. In addition, the glass fiber mats used on the stages to retain particles could not be quantitatively recovered because small slivers were cut from the edges by the spacing rings. Negative weights were obtained from stages with visible deposits.

Particle size data obtained by electron microscopy is presented in Figures 18, 19, and 20. Figures 18 and 19 show the size distribution of particulate material collected on the filter and in the probe during sampling with Method 5. The filter box and probe temperatures during the test (49A) were maintained at 132 and 200 C, respectively. The mean mass diameter of the filter and probe particulate catches are about 0.95 and 1.3 micrometers, respectively.

Figure 20 gives the distribution of particulate material collected on an in-stack flat filter. The sample was collected in Run 49B which was performed concurrently with the Method 5 sampling. The mean mass diameter of the particulates is about 0.6 micrometers.

Photographs of the particulate collections are presented in Figures 21, 22, and 23. The particles collected on both filters, Method 5 and in-stack, have about the same size and morphology. The probe catch is comprised of larger particles and agglomerations of small particles which probably deposited under the influence of gravity.

TABLE 29. IMPINGER COLLECTION DATA

Run No.	System Temperatures, C		Sample Residue Weights, mg		
	Filter Box	Probe	Water (extracted)	Chloroform/Ether	Acetone
21A			116.5	15.8	1.9
21B			277.4	29.4	3.0
23A			109.8	43.0	2.6
23B	121	121	95.9	8.4	2.0
32A	121	121	78.4	13.2	(a)
32B			243.5	11.5	(a)
35A			116.0	20.9	(a)
35B			108.8	14.5	(a)

(a) Sample not analyzed.

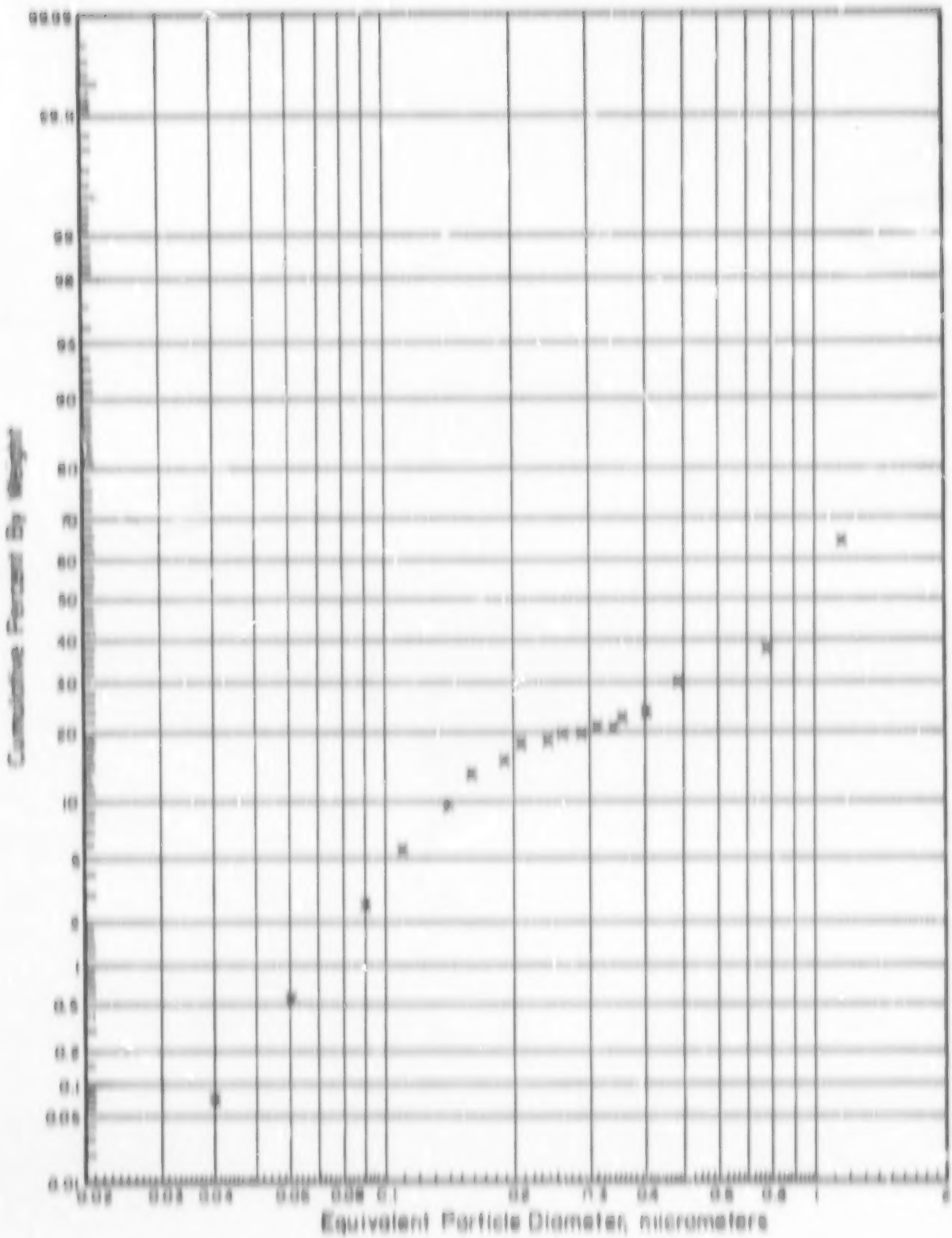


FIGURE 18. PARTICLE SIZE DISTRIBUTION OF FILTER - TOR FROM METHOD 5 SAMPLING OF CEMENT KILN EMISSIONS (RUN 9A)

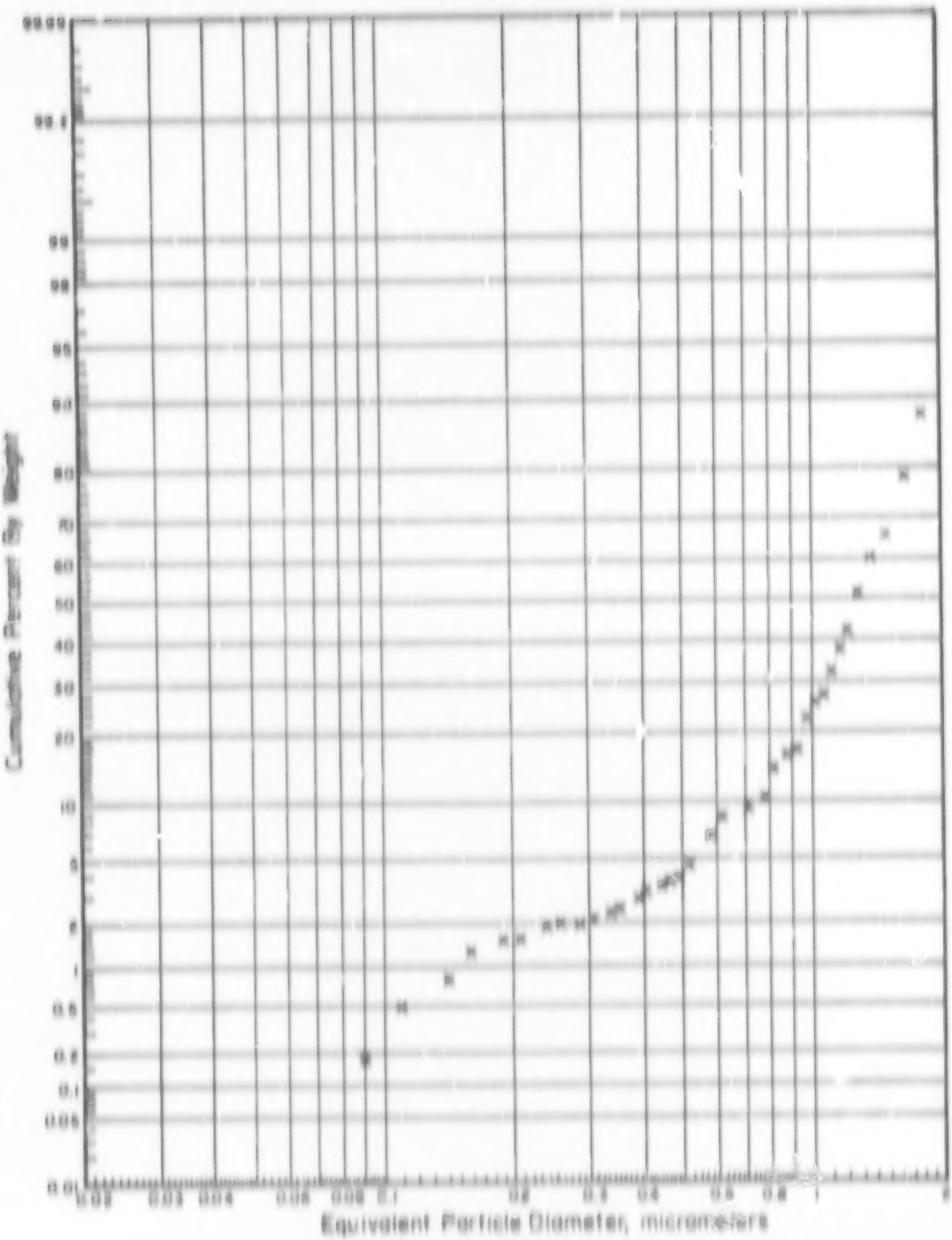


FIGURE 19. PARTICLE SIZE DISTRIBUTION OF PROBE WASH RESIDUE FROM METHOD 5 SAMPLING OF CEMENT KILN EMISSIONS (RUN 49A)

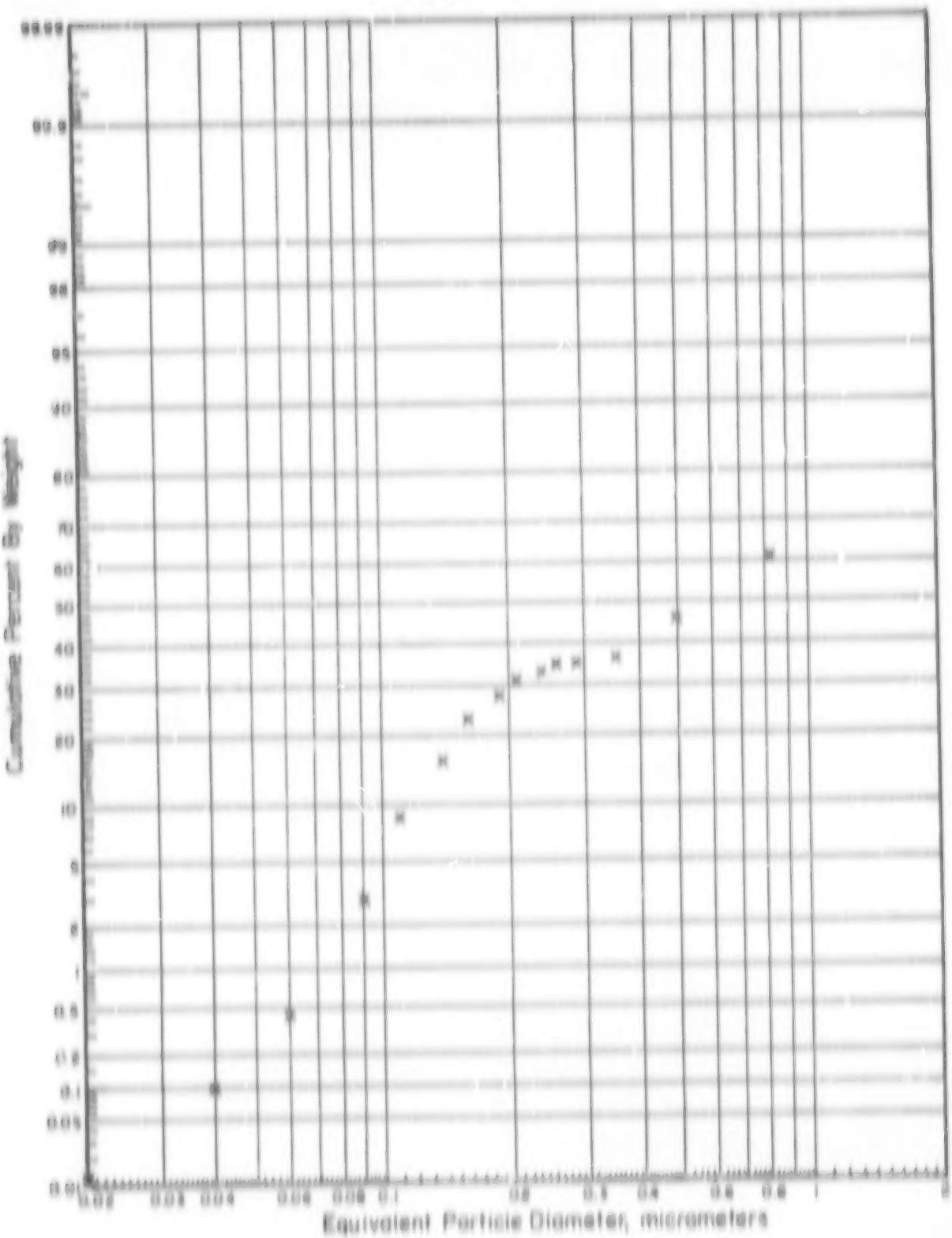


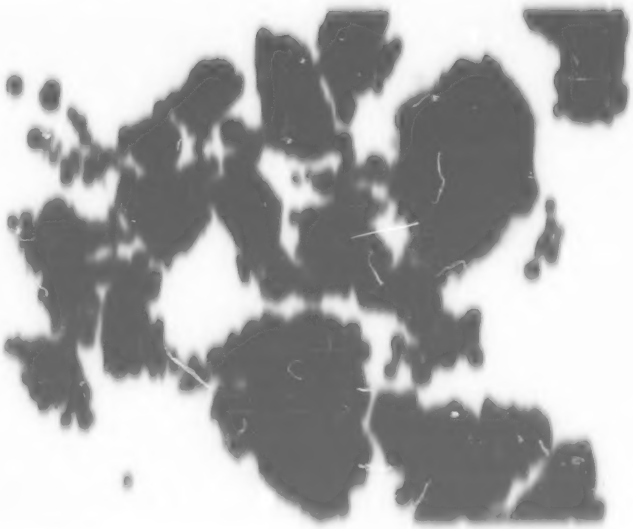
FIGURE 20. PARTICLE SIZE DISTRIBUTION OF FILTER CATCH FROM IN-STACK SAMPLING OF CEMENT KILN EMISSIONS (RUN 4981)

15,000X

15,000X

FIGURE 41. PARTICULATES COLLECTED ON METHOD 5 FILTER (RUN 49A)

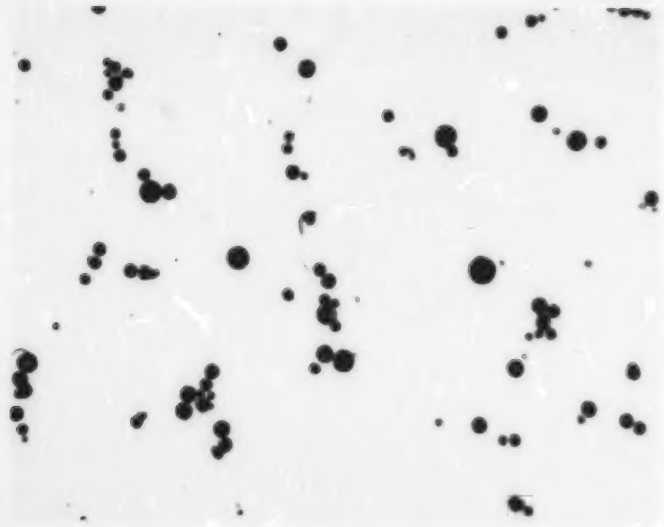
15,000X



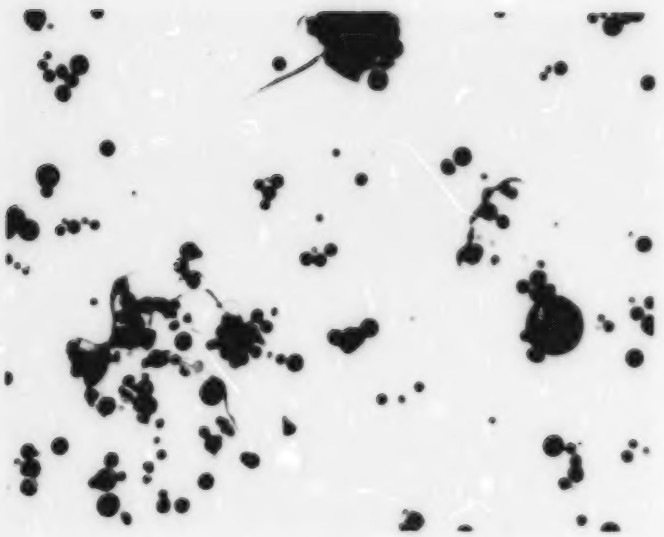
15,000X

15,000X

FIGURE 33. PARTICULATES RETAINED BY METHOD 5 PROBE (RUN 49A)



15,000X



15,000X

FIGURE 23. PARTICULATES COLLECTED ON IN-STACK FLAT FILTER (RUN 49B)

Gas Composition of Kiln Emissions

During initial experiments, continuous monitoring was performed for SO_2 and NO_x (NO and NO_2 combined) to establish concentration ranges in the kiln emissions. A summary of the data are presented in Table 30. The table shows minimum, maximum, and estimated average SO_2 and NO_x concentrations over 11 different 30 to 60-minute sampling periods covering a 3-day interval. The table also includes the results of single CO_2 and O_2 analyses performed during the sampling periods.

The grand average SO_2 and NO_x concentrations are 450 and 535 ppm, respectively. The SO_2 concentration in the emissions exhibits large fluctuations; presumably associated with coal firing rate. Less flucuation was observed in oxides of nitrogen concentration.

Analyses for ammonia and sulfur oxides in the kiln emissions were performed to obtain correlative data on the potential for sulfate formation during particulate sampling. Two measurements of ammonia in the kiln emission obtained on different days gave concentrations of 11 and 18 ppm.

Two SO_2 measurements performed during the same day gave concentrations of 450 and 765 ppm. Both the corresponding sulfuric acid (SO_3) measurements produced results indicating a level less than the minimum detectable concentration, in this case about 0.1 ppm. However, there is a possibility that the sulfuric acid reacted with the quartz wool filter used in the sampling. If the level is similar to that of other coal-fired combustion sources, a sulfuric acid concentration of about 1 percent of the SO_2 concentration would be expected, i.e., about 4 to 8 ppm.

TABLE 30. SUMMARY OF MONITORING FOR GASEOUS COMPONENTS OF CEMENT KILN EMISSIONS

Sampling Period	SO_2 (PPM)			NO_x (PPM)			Per Cent	
	Minimum	Maximum	Average	Minimum	Maximum	Average	CO_2	O_2
1	30	415	176	635	1556	961	23.3	4.8
2	45	132	89	490	600	553	23.7	5.2
3	33	78	55	460	580	515	24.4	4.7
4	~ 0	1000	500	285	570	414	25.5	4.1
5	25	280	173	615	730	669	23.3	5.4
6	260	2340	952	420	780	579	26.0	4.6
7	~ 0	170	81	430	570	495	23.0	5.3
8	360	712	466	310	260	339	25.9	4.1
9	120	870	301	400	663	549	24.1	4.9
10	~ 0	840	425	435	630	501	24.6	4.5
11	960	2260	1715	240	340	315	25.6	3.9

DISCUSSION

Of the sampling system operating parameters investigated in this work, sampling temperature has the most significant effect on mass measurements. Results obtained with Method 5 temperature conditions were up to 43 percent higher than results obtained using a sampling temperature near stack conditions, 205C (400F). Chemical analysis clearly shows that the difference results from ammonium sulfate and/or ammonium bisulfate formation in probe when sampling is performed at the minimum temperature specified by Method 5.

The data presented in Appendix E, Figure E-2 indicates that the minimum sampling temperature specified by Method 5 may not be above the dew point of sulfuric acid, particularly for wet process cement plants which have high moisture content in the emissions. Figures E-3 and E-4 show that if about 2 ppm H_2SO_4 and 15 ppm ammonia are present in the emissions, the sampling temperature must be held above 190C (375F) to prevent formation of ammonium sulfate in the sampling train.

It is apparent that depending on the sampling temperature, different mass emission results can be obtained when sampling the same cement plant. Consequently, Method 5 when applied to cement plants must specify sampling temperature conditions more rigorously. In addition, gas temperature measurements should be made during sampling and care should be exercised in regulating the temperature in order to produce results with satisfactory precision.

Selection of filter materials appears to be another important consideration in measuring particulate emissions from cement plants (and probably other sources with sulfur oxides emissions). The Munktell glass fiber thimble which has a relatively high tare weight compared to flat filters (about 2 grams versus 0.3 grams) also has a correspondingly high content of cations which readily react to form sulfates. Mass emission values obtained with the thimbles averaged 18 percent higher than Method 5 operated at elevated temperature and using MSA 1106 BH filters. However, the results indicate that extraneous sulfate may be formed on the MSA filter medium and may yield mass data which is high by 10 to 16 percent. It is important to note that the sulfate formation occurs well above the dew point of sulfuric acid. Extraneous sulfate formation observed in this study and by others[12, 13] suggests the need for an alternate filter material which is unreactive with sulfur oxides.

The direction and magnitude of errors due to anisokinetic sampling were on the order predicted by previous experimental and theoretical work[14-17]. At 0.7 and 1.3 times isokinetic rate the results deviated from isokinetic mass collections by +5.9 percent and -11.5 percent, respectively. These deviations are not declared highly statistically significant when compared to the normal measurement errors. Sampling within the ± 10 percent range specified by Method 5 should restrict the magnitude of anisokinetic sampling error to an acceptable level.

The comparison of in-stack sampling with MSA 1106 BH filter medium and Method 5 operated at a gas sample temperature of ~205C (401F) and using MSA filters shows that the two methods give equivalent results. In-stack sampling results including only the nozzle and in-stack filter catches were an average of 0.8 percent higher than Method 5 results, a difference which is not statistically significant. Analyses confirm that particulate collections made by the two methods are also equivalent in chemical composition.

In-stack sampling was not compared experimentally with Method 5 operated at the specified minimum gas temperature, 121C (250F). However, it is evident from other experiments which were performed that in this situation Method 5 would give significantly higher mass results.

One advantage of the in-stack technique is that it greatly facilitates sample recovery. The Method 5 probe wash, during which there is potential for sample loss or contamination may be eliminated. In addition, if a backup filter is used, a check is provided on any leakage of the in-stack filter. Use of a backup filter may also prevent invalidation of a source test due to leakage of the primary filter.

Overall, Method 5 appears to be an acceptable procedure to determine mass emissions from cement plants with the exception of the problem of ammonium sulfate formation discussed previously. When sampling is performed by maintaining an elevated gas temperature, the precision of the method appears acceptable, 5.5 percent (repeatability) and the chemical composition of the collections appear to be representative of the particulate material at the sampling location in the stack.

REFERENCES

(1). Federal Register, Volume 36, No. 247, pgs 24876-24895, Thursday, December 23, 1971.

(2). Federal Register, Volume 39, No. 47, pgs 9308-9323, Friday, March 8, 1974.

(3). Federal Register, Volume 39, No. 177, pg 32852, Wednesday, September 11, 1974.

(4). Reference 1, pgs 24888-24890.

(5). Reference 3, page 32856.

(6). Henry, W. M., Howes, J. E., Jr., and Engdahl, R. B., "Evaluation of Particulate Sampling and Analysis Techniques for Cement Plant (Kiln) Emissions", Interim Report No 1, March 8, 1974.

(7). Kreichelt, T. E., Kemnitz, D. A., and Cuffe, S. T., "Atmospheric Emission from the Manufacture of Portland Cement", Public Health Service Publication No. 999-AP-17 (Clearing house Report No PB 190236) 1967.

(8). "Hydrogen Ion Concentration (pH) of Paper Extracts -- Hot Extraction Method", TAPPI Method, T 435 Su-68, Technical Association of the Pulp and Paper Industry, 360 Lexington Avenue, New York, N.Y. 10017.

(9). ASTM Method D 202, 1974 Annual Book of ASTM Standards, Part 20, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103.

(10). Goksóyr, H. and Ross, K., "The Determination of Sulfur Trioxide in Flue Gases", J. Inst. Fuel, 35, pg 177 (1962).

(11). ASTM Method D 3226-73T, 1974 Annual Book of ASTM Standards, Part 26, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103.

(12). Hemeon, W. C. L., and Black, A. W., "Stack Dust Sampling: In-Stack Filter or EPA Train", Journal of the Air Pollution Control Association, 22, pgs. 516-519 (July 1972).

(13). Baum, F. and Riechardt, I., "Measuring Errors occurring during Determination of Trioxide on Measuring Filters" Strub-Reinhalt Luft, 27, pgs 18-22 (September 1967).

(14). Schmel, G. A., "Particle Sampling Bias Introduced by Anisokinetic Sampling and Deposition within the Sample Line", American Industrial Hygiene Association Journal, 31, pgs. 758-771, (November-December 1970).

(15). Vitols, V. "Theoretical Limits of Errors due to Anisokinetic Sampling of Particulate Matter", Journal of the Air Pollution Control Association, 16, pgs. 79-84 (February 1966).

(16). Hemeon, W. C. L., and Haines, G. F., "The Magnitude of Errors in Stack Dust Sampling", Air Repair, 4, pg 159 (1954).

(17). Badzioch, "Correction of Anisokinetic Sampling of Gas-Borne Dust Particles", Journal of the Institute of Fuels, 33, pg 106 (1960).

APPENDIX A

METHOD 5 - DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

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Thursday, December 23, 1971

APPENDIX-A

RULES AND REGULATIONS

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and its weight is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling train. The design specifications of the particulate sampling train used by EPA (Figure 5-1) are described in APTD-0581. Commercial models of this train are available.

2.1.1 Nozzle—Stainless steel (316) with sharp, tapered leading edge.

2.1.2 Probe—Pyrex[1] glass with a heating system capable of maintaining a minimum gas temperature of 250° F. at the exit end during sampling to prevent condensation from occurring. When length limitations (greater than about 8 ft.) are encountered at temperatures less than 600° F., Incoloy 825[1], or equivalent, may be used. Probes for sampling gas streams at temperatures in excess of 600° F. must have been approved by the Administrator.

2.1.3 Pitot tube—Type S, or equivalent, attached to probe to monitor stack gas velocity.

2.1.4 Filter Holder—Pyrex[1] glass with heating system capable of maintaining minimum temperature of 225° F.

2.1.5 Impingers / Condenser—Four impingers connected in series with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design, modified by replacing the tip with a ½-inch ID glass tube extending to one-half inch from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip. A condenser may be used in place of the impingers provided that the moisture content of the stack gas can still be determined.

2.1.6 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5° F., dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer—To measure atmospheric pressure to ±0.1 inches Hg.

2.2 Sample recovery.

2.2.1 Probe brush—At least as long as probe.

2.2.2 Glass wash bottles—Two.

2.2.3 Glass sample storage containers.

2.2.4 Graduated cylinder—250 ml.

2.3 Analysis.

2.3.1 Glass weighing dishes.

2.3.2 Desiccator.

2.3.3 Analytical balance—To measure to ±0.1 mg.

2.3.4 Trip balance—300 g. capacity, to measure to ±0.05 g.

3. *Reagents.*

3.1 Sampling.

3.1.1 Filters—Glass fiber, MSA 1106 BH[1], or equivalent, numbered for identification and preweighed.

3.1.2 Silica gel—Indicating type, 6–16 mesh, dried at 175° C. (350° F.) for 2 hours.

3.1.3 Water.

3.1.4 Crushed ice.

3.2 Sample recovery.

3.2.1 Acetone—Reagent grade.

3.3 Analysis.

3.3.1 Water.

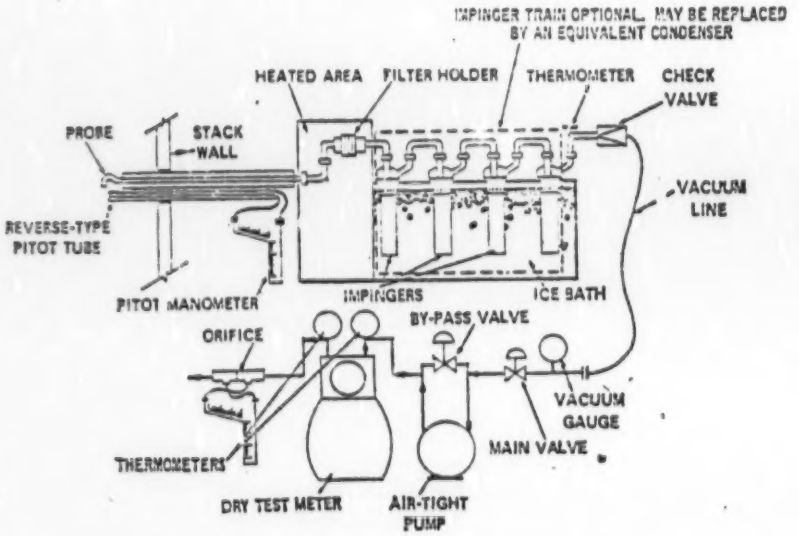

Figure 5-1. Particulate-sampling train.

3.3.2 Desiccant—Drierite,[2] indicating.

4. *Procedure.*

4.1 Sampling

4.1.1 After selecting the sampling site and the minimum number of sampling points, determine the stack pressure, temperature, moisture, and range of velocity head.

4.1.2 Preparation of collection train. Weigh to the nearest gram approximately 200 g. of silica gel. Label a filter of proper diameter, desiccate[2] for at least 24 hours and weigh to the nearest 0.5 mg. in a room where the relative humidity is less than 50%. Place 100 ml. of water in each of the first two impingers, leave the third impinger empty, and place approximately 200 g. of preweighed silica gel in the fourth impinger. Set up the train without the probe as in Figure 5-1. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 15 in. Hg vacuum. A leakage rate not in excess of 0.02 c.f.m. at a vacuum of 15 in. Hg is acceptable. Attach the probe and adjust the heater to provide a gas temperature of about 250° F. at the probe outlet. Turn on the filter heating system. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger as low as possible and preferably at 70° F., or less. Temperatures above 70° F. may result in damage to the dry gas meter from either moisture condensation or excessive heat.

4.1.3 Particulate train operation. For each run, record the data required on the example sheet shown in Figure 5-2. Take readings at each sampling point, at least every 5 minutes, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in section 4.2.

[1] Trade name.

[2] Dry using Drierite[1] at 70° F. ±10° F.

PLANT _____
LOCATION _____
OPERATOR _____
DATE _____
RUN NO. _____
SAMPLE BOX NO. _____
METER BOX NO. _____
METER ΔH_2 _____
C FACTOR _____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE _____
BAROMETRIC PRESSURE _____
ASSUMED MOISTURE, % _____
HEATER BOX SETTING _____
PROBE LENGTH, in. _____
NOZZLE DIAMETER, in. _____
PROBE HEATER SETTING _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE (P_s), in. Hg	STACK TEMPERATURE (T_s), °F	VELOCITY HEAD (Δp), in. H₂O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH), in. H₂O	GAS SAMPLE VOLUME (Corrected), ft³	GAS SAMPLE TEMPERATURE AT DRY GAS METER: INLET ($T_{m_{in}}$), °F	GAS SAMPLE TEMPERATURE AT DRY GAS METER: OUTLET ($T_{m_{out}}$), °F	SAMPLE BOX TEMPERATURE, °F	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °F
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

Figure 5-2. Particulate field data.

4.2 Sample recovery. Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. Measure the volume of water from the first three impingers, then discard. Place the samples in containers as follows:

Container No. 1. Remove the filter from its holder, place in this container, and seal.

Container No. 2. Place loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter in this container and seal. Use a razor blade, brush, or rubber policeman to lose adhering particles.

Container No. 3. Transfer the silica gel from the fourth impinger to the original container and seal. Use a rubber policeman as an aid in removing silica gel from the impinger.

4.3 Analysis. Record the data required on the example sheet shown in Figure 5-3. Handle each sample container as follows:

Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish, desiccate, and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 2. Transfer the acetone washings to a tared beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 3. Weigh the spent silica gel and report to the nearest gram.

5. *Calibration.*

Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater. Recalibrate after each test series.

6. *Calculations.*

6.1 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.2 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F., 29.92 inches Hg) by using Equation 5-1.

$$V_{m_{std}} = V_m\left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{P_{std}}\right) = \left(17.71\ \frac{°R}{in.\ Hg}\right)V_m\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{T_m}\right)$$

equation 5-1

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

ΔH = Average pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.3 Volume of water vapor.

$$V_{w_{std}} = V_{l_c}\left(\frac{\rho_{H_2O}}{M_{H_2O}}\right)\left(\frac{RT_{std}}{P_{std}}\right) = \left(0.0474\ \frac{cu.\ ft.}{ml.}\right)V_{l_c}$$

equation 5-2

where:

$V_{w_{std}}$ = Volume of water vapor in the gas sample (standard conditions), cu. ft.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

ρ_{H_2O} = Density of water, 1 g./ml.

M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.

R = Ideal gas constant, 21.83 inches Hg—cu. ft./lb.-mole-°R.

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.4 Moisture content.

$$B_{ws} = \frac{V_{w_{std}}}{V_{m_{std}} + V_{w_{std}}}$$

equation 5-3

where:

B_{ws} = Proportion by volume of water vapor in the gas stream, dimensionless.

$V_{w_{std}}$ = Volume of water in the gas sample (standard conditions), cu. ft.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

6.5 Total particulate weight. Determine the total particulate catch from the sum of the weights on the analysis data sheet (Figure 5-3).

6.6 Concentration.

6.6.1 Concentration in gr./s.c.f.

$$c'_s = \left(0.0154\frac{gr.}{mg.}\right)\left(\frac{M_n}{V_{m_{std}}}\right)$$

equation 5-4

where:

c'_s = Concentration of particulate matter in stack gas, gr./s.c.f., dry basis.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

PLANT _____

DATE _____

RUN NO. _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER. (1 g. ml):

$$\frac{\text{INCREASE, g}}{(1\ \text{g/ml})} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

6.6.2 Concentration in lb./cu. ft.

$$c_s = \frac{\left(\frac{1}{453{,}600}\frac{\text{lb.}}{\text{mg.}}\right)M_n}{V_{m_{std}}} = 2.205\times10^{-6}\frac{M_n}{V_{m_{std}}} \qquad \text{equation 5-5}$$

where:

c_s = Concentration of particulate matter in stack gas, lb./s.c.f., dry basis.

453,600 = Mg/lb.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

6.7 Isokinetic variation.

$$I = \frac{T_s\left[\frac{V_{l_c}(\rho_{H_2O})R}{M_{H_2O}} + \frac{V_m}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n} \times 100$$

$$= \frac{\left(1.667\frac{\text{min.}}{\text{sec.}}\right)\left[\left(0.00267\frac{\text{in. Hg-cu. ft.}}{\text{ml.-}^\circ\text{R}}\right)V_{l_c} + \frac{V_m}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n} \qquad \text{Equation 5-6}$$

where:

I = Percent of isokinetic sampling.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (See Fig. 5-3), ml.

ρ_{H_2O} = Density of water, 1 g./ml.

R = Ideal gas constant, 21.83 inches Hg-cu. ft./lb. mole-°R.

M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °R.

P_{bar} = Barometric pressure at sampling site, inches Hg.

ΔH = Average pressure drop across the orifice (see Fig. 5-2), inches H_2O.

T_s = Absolute average stack gas temperature (see Fig. 5-2), °R.

θ = Total sampling time, min.

V_s = Stack gas velocity calculated by Method 2, Equation 2-2, ft./sec.

P_s = Absolute stack gas pressure, inches Hg.

A_n = Cross-sectional area of nozzle, sq. ft.

6.9 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If $90\% \leq I \leq 110\%$, the results are acceptable, otherwise, reject the results and repeat the test.

7. *Reference.*

Addendum to Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, Dec. 6, 1967.

Martin, Robert M., Construction Details of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0581.

Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, Environmental Protection Agency APTD-0576.

Smith, W. S., R. T. Shigehara, and W. F. Todd, A Method of Interpreting Stack Sampling Data, Paper presented at the 63d Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14-19, 1970.

Smith, W. S., et al., Stack Gas Sampling Improved and Simplified with New Equipment, APCA paper No. 67-119, 1967.

Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, 1967.

APPENDIX B

STACK GAS MEASUREMENT DATA

APPENDIX B

TABLE B-1. STACK GAS DATA - ANISOKINETIC STUDY

Run No.	$\sqrt{\Delta P}$ (avg), cm $H_2O^{\frac{1}{2}}$	T_s (avg), C	P_s, mm Hg	O_2, %	CO_2, %	B_{wo}, %	M_d, lb/lb-mole	V_s (avg), m/s
1A	1.12	203	722.9	8.5	18.5	32.94	31.3	16.0
B						32.86		
2A	1.13	212	722.6	8.5	18.5	31.87	31.3	16.3
B						31.77		
3A	1.13	213	725.6	8.5	18.5	32.20	31.3	16.3
B						32.00		
4A	1.12	222	724.9	8.5	18.5	30.56	31.3	16.3
B						30.97		
5A	1.10	223	725.2	8.5	18.5	30.54	31.3	15.9
B						30.23		
6A	1.08	222	724.4	8.5	18.5	31.09	31.3	15.9
B						30.03		
7A	1.08	218	723.6	8.5	18.5	30.61	31.3	15.8
B						30.38		
8A	1.07	223	721.9	8.5	18.5	31.37	31.3	15.6
B						31.07		
9A	1.08	220	722.1	8.5	18.5	32.70	31.3	15.8
B						31.17		
10A	1.05	220	720.6	8.5	18.5	31.03	31.3	15.4
B						30.21		
11A	1.07	221	723.4	8.5	18.5	32.66	31.3	15.5
B						32.81		
12A	1.10	221	723.1	8.5	18.5	31.22	31.3	15.9
B						30.72		
13A	1.12	222	722.1	8.5	18.5	30.21	31.3	16.3
B						29.40		
14A	1.12	217	722.9	8.5	18.5	32.92	31.3	16.3
B						32.48		
15A	1.08	223	721.4	8.5	18.5	29.71	31.3	15.7
B						29.81		
16A	1.10	222	720.1	8.5	18.5	30.05	31.3	16.1
B						29.48		

TABLE B-2. STACK GAS DATA-FILTER SIZE, TEMPERATURE, AND NOZZLE CONFIGURATION EXPERIMENTS

Run No.	$\sqrt{-P}$ (avg), cm $H_2O^{\frac{1}{2}}$	T_s (Avg), C	P_s, mm HG	O_2, %	CO_2, %	B_{wo} %	M_d, lb/lb-mole	V_s (avg), m/s
17A	1.13	209	717.3	7.0	18.0	31.84	31.2	16.4
B						31.92		
18A	1.15	211	716.5	7.0	18.0	32.46	31.2	16.6
B						31.94		
19A	1.04	214	715.5	7.0	18.0	31.12	31.2	15.2
B						31.18		
21A	1.13	214	713.7	7.0	18.0	32.36	31.2	16.6
B						32.31		
22A	1.16	211	712.7	7.0	18.0	32.24	31.2	16.9
B						32.35		
23A	1.15	198	714.2	7.0	18.0	34.10	31.2	16.6
B						32.88		
24A	1.08	205	714.2	7.0	18.0	31.97	31.2	15.6
B						31.49		
25A	1.13	203	713.5	7.0	18.0	33.49	31.2	16.3
B						32.62		
27A	1.07	221	717.6	7.0	18.0	29.83	31.2	15.5
B						29.65		
28A	1.10	213	716.3	7.0	18.0	31.82	31.2	15.9
B						31.58		
29A	1.10	207	718.6	7.0	18.0	31.82	31.2	15.8
B						31.15		
31A	1.13	206	718.1	7.0	18.0	31.76	31.2	16.2
B						32.00		

TABLE B-3. STACK GAS DATA-PROBE/BOX FILTER TEMPERATURE EXPERIMENTS

Run No.	$\sqrt{\Delta P}$ (avg), cm $H_2O^{\frac{1}{2}}$	T_s (avg), C	P_s, mm Hg	O_2, %	CO_2, %	B_{wo}, %	M_d, lb/lb-mole	V_s (avg), m/s
32A	1.08	194	714.2	.0	18.0	31.49	31.2	15.0
B						30.27		
33A	1.00	204	713.7	8.0	18.0	30.27	31.2	14.4
B						28.91		
34A	1.08	189	713.7	8.0	18.0	30.17	31.2	14.8
B						29.41		
35A	1.00	204	713.0	8.0	18.0	28.23	31.2	14.3
B						27.76		
36A	1.08	188	713.0	8.0	18.0	32.01	31.2	14.8
B						31.50		
37A	1.08	190	712.7	8.0	18.0	30.50	31.2	14.8
B						30.72		
38A	1.04	199	712.5	8.0	18.0	30.24	31.2	14.9
B						30.74		
39A	1.08	189	713.7	8.0	18.0	30.75	31.2	14.9
B						30.98		
40A	1.08	188	714.2	8.0	18.0	29.51	31.2	14.8
B						30.40		

TABLE B-4. STACK GAS DATA-IN-STACK FILTER EXPERIMENTS

Run No.	$\sqrt{\Delta P}$ (avg), cm $H_2O^{\frac{1}{2}}$	T_s (avg), C	P_s, mm Hg	O_2, %	CO_2, %	B_{wo}, %	M_d, lb/lb-mole	V_s (avg), m/s
41A	1.18	232	720.9	8.5	19.0	31.01	31.4	17.4
B						31.38		
42A	1.13	236	720.3	8.5	19.0	31.34	31.4	16.8
B						31.36		
43A	1.15	226	718.6	8.5	19.0	31.33	31.4	16.8
B						31.71		
44A	1.13	230	720.3	7.0	19.0	32.00	31.3	16.7
B						32.62		
45A	1.13	228	721.1	7.0	19.0	32.10	31.3	16.7
B						32.33		
46A	1.16	225	720.6	6.0	19.5	31.95	31.4	17.1
B						32.27		
47A	1.16	222	723.4	6.0	20.5	32.37	31.5	17.0
B						33.05		
48A	1.16	226	723.4	6.0	20.5	32.18	31.5	16.9
B						32.29		
49A	1.16	223	721.9	5.5	22.5	31.68	31.8	16.9
B						32.08		

APPENDIX C

SAMPLING SYSTEM OPERATION DATA

TABLE C-1. SAMPLING DATA - ANISOKINETIC SAMPLING EXPERIMENTS

Run No	Meter Volume (V_m), m^3	Barometer, mm Hg	ΔH, mm H_2O	Avg. Meter Temp (T_m), C	Dry Gas Sampled Std Cond, (V_{mstd}), m^3	Percent Isokinetic	Average System Temperatures, C: Filter Box	Gas @ Probe Outlet	Probe Mid-Point
1A	2.37	741.9	41.4	32	2.24	106	127	129	--
B	1.67	741.9	18.3	29	1.59	75	123	126	79
2A	2.45	741.7	41.9	32	2.31	107	122	124	--
B	2.42	741.7	38.1	33	2.28	106	129	126	52
3A	1.67	744.7	19.3	34	1.57	73	126	127	--
B	2.29	744.7	35.1	37	2.14	99	120	124	77
4A	2.28	744.0	38.4	38	2.12	98	124	133	--
B	3.04	744.0	60.5	39	2.82	131	127	127	116
5A	2.31	744.2	37.9	33	2.18	103	126	134	--
B	1.62	744.2	16.3	28	1.55	73	122	122	99
6A	2.31	743.5	37.1	34	2.16	104	124	136	--
B	2.30	743.5	33.3	32	2.18	103	128	126	72
7A	2.98	742.7	62.7	37	2.78	132	128	121	--
B	2.98	742.7	55.9	32	2.82	134	123	122	102
8A	1.61	740.9	17.8	33	1.51	74	122	123	--
B	1.59	740.9	16.0	24	1.54	75	120	122	92
9A	1.62	741.2	18.0	38	1.50	74	124	121	--
B	1.63	741.2	16.3	26	1.57	76	124	124	98
10A	2.93	739.7	59.9	41	2.69	133	123	124	--
B	2.95	739.7	53.9	32	2.78	136	127	124	103
11A	2.23	742.4	35.6	29	2.12	107	126	129	--
B	2.91	742.4	54.6	32	2.76	139	121	124	104
12A	2.97	742.2	63.5	33	2.81	135	126	123	--
B	2.32	742.2	33.8	33	2.18	104	124	124	76
13A	2.35	741.2	39.1	35	2.20	102	123	123	--
B	2.41	741.2	35.8	33	2.26	104	122	125	74
14A	3.00	741.9	66.6	33	2.84	135	123	129	--
B	2.37	741.9	35.8	31	2.24	106	124	130	81
15A	2.30	740.4	36.8	33	2.15	103	125	129	--
B	2.34	740.4	33.0	38	2.16	103	122	128	95
16A	1.65	739.1	18.8	34	1.54	72	122	124	--
B	2.38	739.1	34.8	36	2.21	103	124	128	77

TABLE C-2. SAMPLING DATA - FILTER SIZE, TEMPERATURE, AND NOZZLE CONFIGURATION EXPERIMENTS

Run No	Meter Volume (V_m), m^3	Barometer, mm Hg	ΔH, mm H_2O	Avg. Meter Temp (T_m), C	Dry Gas Sampled Std Cond. (V_{mstd}), m^3	Percent Isokinetic	Average System Temperatures, C		
							Filter Box	Gas @ Probe Outlet	Probe Mid-Point
17A	2.41	742.7	42.2	33	2.27	105	209	210	--
B	2.49	742.7	39.6	38	2.31	107	211	218	188
18A	2.52	741.9	43.4	34	2.31	106	128	131	--
B	2.54	741.9	40.9	41	2.33	107	212	211	173
19A	2.21	740.9	36.1	37	2.05	106	216	218	--
B	2.22	740.9	32.5	38	2.05	106	123	123	79
21A	2.46	739.1	42.4	34	2.30	108	215	221	--
B	2.48	739.1	38.1	35	2.31	108	212	212	178
22A	2.51	738.1	44.7	35	2.34	107	126	127	--
B	2.54	738.1	40.1	36	2.36	108	125	126	88
23A	2.48	739.7	45.0	26	2.38	111	211	208	--
B	2.52	739.7	40.1	23	2.44	111	124	125	91
24A	2.30	739.7	38.4	29	2.19	106	122	123	--
B	2.40	739.7	35.1	28	2.28	110	211	204	162
25A	2.46	738.9	40.6	31	2.32	110	211	212	--
B	2.47	738.9	38.4	27	2.36	110	124	125	81
27A	2.27	743.0	36.8	29	2.16	106	123	133	--
B	2.29	743.0	33.0	33	2.16	105	126	128	84
28A	2.38	741.7	40.6	31	2.25	108	215	216	--
B	2.42	741.7	36.6	38	2.24	107	124	138	82
29A	2.34	744.0	39.9	25	2.27	108	124	127	--
B	2.37	744.0	36.1	26	2.29	108	211	211	163
31A	2.43	743.5	42.7	31	2.31	107	123	126	--
B	2.47	743.5	38.4	29	2.36	109	215	209	155

TABLE C-3. SAMPLING DATA - PROBE/BOX FILTER TEMPERATURE EXPERIMENTS

Run No	Meter Volume (V_m), m^3	Barometer, mm Hg	ΔH mm H_2O	Avg. Meter Temp (T_m), C	Dry Gas Sampled Std Cond. (V_{mstd}), m^3	Percent Isokinetic	Average System Temperatures, C			
							Filter Box	Gas @ Filter Outlet	Gas @ Probe Outlet	Probe Mid-Point
32A	2.23	739.7	35.6	35	2.08	102	122	112	127	--
B	2.27	739.7	30.0	37	2.10	102	206	187	188	161
33A	2.19	739.1	33.8	32	2.05	105	124	108	127	--
B	2.17	739.1	27.9	27	2.07	104	124	157	198	180
34A	2.29	739.1	36.6	31	2.16	104	205	200	201	--
B	2.33	739.1	32.3	27	2.23	106	122	113	124	79
35A	2.21	738.4	34.3	32	2.07	104	207	194	204	--
B	2.21	738.4	35.1	32	2.08	103	125	160	196	175
36A	2.25	738.4	36.8	32	2.12	104	123	165	198	--
B	2.27	738.4	37.9	32	2.14	105	125	116	122	78
37A	2.31	738.1	38.1	29	2.19	106	126	112	122	--
B	2.31	738.1	38.4	32	2.17	105	204	194	189	157
38A	2.31	737.9	38.1	29	2.19	107	123	162	200	--
B	2.28	737.9	38.4	31	2.15	106	203	196	202	172
39A	2.32	739.1	38.6	28	2.21	107	196	193	201	--
B	2.32	739.1	38.9	33	2.18	106	123	154	188	177
40A	2.33	739.7	38.6	28	2.22	106	123	112	126	--
B	2.33	739.7	39.1	36	2.16	104	123	168	191	184

TABLE C-4. SAMPLING DATA-IN-STACK FILTER EXPERIMENTS

Run No.	Meter Volume (V_m), M^3	Barometer, mm Hg	ΔH, mm H_2O	Meter Temp. T_m, C (Ave)	Dry Gas Volume Std Cond. (V_{mstd}), m^3	Percent Isokinetic	Average System Temperatures, C			
							Filter Box	Gas @ Box Filter Outlet	Gas @ Probe Outlet	In-Stack Filter
41A	2.48	741.2	45.5	29	2.36	107	127	167	204	231
B	2.49	741.2	46.7	31	2.36	106	130	167	206	231
42A	2.41	740.7	41.9	33	2.26	107	139	169	210	236
B	2.38	740.7	41.9	34	2.23	104	134	179	192	236
43A	2.44	738.9	42.2	33	2.29	106	129	165	206	226
B	2.44	738.9	43.9	33	2.29	105	136	172	206	226
44A	2.41	740.7	42.7	27	2.31	109	136	166	208	230
B	2.43	740.7	43.9	33	2.29	108	139	182	211	230
45A	2.41	741.4	42.4	33	2.26	107	132	172	206	228
B	2.44	741.4	43.9	32	2.31	108	138	176	210	228
46A	2.48	740.9	44.7	32	2.34	107	137	177	210	225
B	2.54	740.9	46.0	37	2.35	107	132	176	207	225
47A	2.45	743.5	44.7	27	2.36	109	133	171	20	222
B	2.47	743.5	45.7	35	2.32	107	135	171	206	222
48A	2.47	743.7	43.7	33	2.33	108	137	168	207	226
B	2.51	743.7	45.7	33	2.38	109	134	181	206	226
49A	2.48	742.2	44.7	33	2.33	107	132	167	206	224
B	2.53	742.2	46.2	37	2.35	108	139	176	204	224

APPENDIX D

STATISTICAL DESIGN OF EXPERIMENTS TO STUDY SAMPLING METHODOLOGY

APPENDIX D

Experimental Design For The Study

The sampling location used in the field studies permitted the use of only two ports at which sampling nozzles could be located in close proximity. Thus, the number of samples which could be collected concurrently was limited to two. On the other hand, the number of combinations of experimental conditions to be investigated was always greater than two. Because stack conditions can vary substantially over time, experimental combinations effects which may be significant would be confounded with the variations in the stack conditions. One method of avoiding this problem is to use statistical designs for the experiment which selectively confound particular factor effects with the variations in stack conditions, or which handle data where not all experimental combinations are tested concurrently. Two such designs were used for this study -- an incomplete randomized block design and a confounded factorial design. The purpose of this appendix is to describe these designs and to discuss the manner in which their calculational methods differ from the standard analysis of variance methods.

Incomplete Randomized Block Design[1]

In experimental design discussions, it is common practice to speak of "treatment" combination. The term "treatment" is intended to mean any controlled variation in experimental conditions. (In the present study, for example, the use of in-stack flat filter versus the use of an in-stack thimble filter may be thought of as two treatments). Usually, experiments are designed so that data on all treatment levels are collected within one statistical block where the term "block" indicates simultaneous collection of data or some such arrangement for keeping error variance as small as possible.

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(1) Davies, Owen L., Editor, The Design and Analysis of Industrial Experiments, Hafner Publishing Company, New York (1960), Chapter 6.

When there is only one experimental factor being investigated (e.g., type of filter), and there are more treatment levels of that factor than can be compared at one time, and all comparisons are equally important, an incomplete randomized block design can be used to plan the experiment. For this study, several experiments involved only one factor (such as filter type) with three levels of treatment which could only be employed two at a time. In these experiments, every pair of treatment combinations was repeated three times. Since there were three pairs of treatment combinations, nine statistical blocks of data were collected. These blocks were structured so that every pair of treatment combinations appeared an equal number of times (thus assuring balance) and then the order in which the blocks were run was randomized. This produces the incomplete randomized block design needed. As an example, the data collected from such a design can be represented in the form shown in Table D-1, where a dash indicates no data for one of the treatment levels within the block and the X's indicate data. Row sums and column sums of this table represent totals of observations for particular blocks (B) or treatments (T), while G indicates the grand total of all 18 observations.

In order to present the calculational methods for this design, the following notation is necessary:

t = the number of treatment levels

r = the number of replications of each treatment level

b = the number of statistical blocks

k = the number of experimental units per block

N = the number of observations.

For this study, $t = 3$, $r = 6$, $b = 9$, $k = 2$, and $N = tr = bk = 18$.

To calculate the treatment effects Davies indicates that one must

(1) first calculate, for each treatment,

$Q_i = kT_i$ - (Sum of totals for all blocks containing the $i^{\underline{th}}$ treatment); then

(2) obtain $P_i = \dfrac{Q_i}{N(k-1)/(t-1)}$,

where the P_i terms are the estimated treatment effects, or more correctly the estimated deviations of particular treatment effects from the average effect of all treatments used in the experiment. Thus the corrected or adjusted mean for the $i^{\underline{th}}$ treatment can be calculated as the grand mean (G/N) plus P_i. This sum represents an estimate of the $i^{\underline{th}}$ treatment mean one would observe if all treatments had been used in every block.

TABLE D-1. BALANCED INCOMPLETE BLOCK DESIGN FOR THREE REPLICATIONS OF AN EXPERIMENT WITH THREE TREATMENT LEVELS OCCURRING IN BLOCKS OF TWO.

Block	Treatment 1	2	3	Total
1	-	X	X	B_1
2	X	-	X	B_2
3	X	X	-	B_3
4	-	X	X	B_4
5	X	-	X	B_5
6	X	X	-	B_6
7	-	X	X	B_7
8	X	-	X	B_8
9	X	X	-	B_9
Total T_i	T_1	T_2	T_3	G
Intermediate Adjustment Factor	Q_1	Q_2	Q_3	0.0
Estimated Deviations of Treatment Effects From Grand Average	P_1	P_2	P_3	0.0

The calculational formulae for the Analysis of Variance Table resulting from this design are presented in Table D-2. The interpretation of this table follows that for the usual analysis of variance except that one is usually not interested in testing for significance between blocks.

Comparisons between any two particular treatment means can be made by calculating the standard deviation of the difference between the corrected means of any two treatments as

$$S\sqrt{\frac{2k(t-1)}{N9k-1)}} \quad ,$$

multiplying this standard deviation by the critical value of the Student's t - distribution for (N-t-b+1) degrees of freedom and a chosen confidence level, and comparing the result to the difference in the treatment means. Any difference which exceeds this result would be declared statistically significant at the chosen confidence level.

Confounded Factorial Design[2]

This type of design represents the most efficient way of dealing with a situation where several experimental factors are to be investigated simultaneously and the resulting number of combinations of treatment levels of these factors is larger than the number of combinations which can be carried out under uniform test conditions. For example such a problem existed in this study in investigating the effect of filter size on the sampling system while at the same time testing for significant effects due to temperature and nozzle type. With each of these factors having two treatment levels, there were eight treatment combinations which could only be run in blocks of two at a time.

The confounded factorial design divides the experiment into smaller blocks in a particular manner, such that the more important effects of the factors can be investigated under uniform test conditions (i.e. through concurrent measurement) while the less important effects are confounded with variations between blocks.

A discussion of the procedures used to develop the confounded designs is based upon mathematical concepts of modulus arithemetic. The interested reader is referred to Davies. The experimental designs which are presented

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(2) See Davies, Chapter 9.

TABLE D-2. ANALYSES OF VARIANCE FOR BALANCED INCOMPLETE BLOCK DESIGN OF EXPERIMENTS

Source of Variation	Sum of Squares of Deviations	Degrees of Freedom	Mean Squares
Between Corrected Treatment Totals	$\frac{(t-1)}{Nk(k-1)} \sum_{i=1}^{t} Q_i^2$	(t-1)	$\frac{\text{Sum of Squares}}{\text{Degrees of Freedom}}$
Between Actual Block Totals	$\frac{\sum_{j=1}^{b} B_j^2}{k} - \frac{G^2}{N}$	(b-1)	(Discard)
Remainder	Difference	(N-t-b+1)	$\frac{\text{Sum of Squares}}{\text{Degrees of Freedom}}$
Total	$\sum_{i=1}^{t} \sum_{j=1}^{b} X_{ij}^2 - \frac{G^2}{N}$	(N-1)	

in this report were developed using such concepts. Because the number of statistical blocks of data which were collected was sufficiently large, it was possible to partially confound selected factors rather than completely confound factors. By this method, the confounded factors were only confounded in selected blocks of data, and their effects could still be estimated from the remaining blocks in which they were not confounded. The factors and the blocks in which they were confounded have been identified in the tables in the main body of this report. The calculational methods for this partially confounded factorial design are performed in the same manner as is done for the standard analyses of variance design with one exception. The exception is that any data from a block which is confounded with a particular factor are excluded from the calculation of the sums of squares of deviations for that factor.

APPENDIX E

CONDENSATION OF SULFURIC ACID AND AMMONIUM SULFATE UNDER VARIOUS CONDITIONS ENCOUNTERED IN CEMENT PLANT EMISSIONS

APPENDIX E

Sulfuric Acid Dewpoint

The dewpoint of a vapor is defined as that temperature at which vapor of a given composition is in equilibrium with a condensed liquid phase. In the case of the condensation of sulfuric acid from flue gas, this involves both water vapor and sulfuric acid vapor in equilibrium with sulfuric acid containing water, viz.,

$$H_2SO_4(aq) \rightleftharpoons H_2O(v) + H_2SO_4(v). \qquad (1)$$

Both the composition of the liquid phase and the dewpoint in such a system are functions of the overall initial composition of the vapor, and the equilibrium constant can be expressed as

$$K' = (P_{H_2O} P_{H_2SO_4}) / (N_{H_2O} N_{H_2SO_4}) \qquad (2)$$

where P_i and N_i represent the partial pressure and mole fraction in the liquid phase for each component. Inasmuch as sulfuric acid compositions are usually expressed in terms of weight fractions rather than mole fractions, it is convenient at this point to express the equilibrium constant in terms of C, the weight fraction of sulfuric acid in the liquid phase.

$$K = (P_{H_2O} P_{H_2SO_4}) / [C(1-C)] \qquad (3)$$

This equilibrium constant can then be related to the dewpoint of the vapor by

$$\ln K = A - \Delta H/RT \qquad (4)$$

where ΔH is the enthalpy change for the process and A is a constant that is related to the entropy change. Müller[1] has examined in detail the thermodynamics of the sulfur acid/water system, and has derived a rigorous approach to calculation of dewpoints based on the temperature dependencies of various components of A and ΔH in Equation (4). However, it can be shown that existing vapor pressure and dewpoint data can be adequately predicted with such a correlation over a wide range of sulfuric acid/water compositions.

While a number of reports of dewpoints and total vapor pressures over

(1) Müller, P.E., "A Contribution to the Problem of Sulfuric Acid on the Dew Point Temperature of Flue Gases", Chem. Ing. Tech. 31, pgs 345-351 (1959).

sulfuric acid solutions are in the literature, only in a few cases is it possible to either cite or infer the individual partial pressures of water and sulfuric acid. The following is therefore based primarily on data given by Abel[2] and by Lisle and Sensenbaugh[3]. Figure E-1 shows a semilogrithmic plot values of K calculated from these two sources as a function of the inverse of the temperature. Units employed in this plot are torr, weight percent, and degrees Kelvin. It can be seen that the simple form of Equation (4) does represent these data over approximately an eight-decade range of the equilibrium constants. A least-squares fit of Equation (4) to these data yields

$$\log A = 19.580 \pm 0.18 \text{ and } \Delta H = 35{,}500 \pm 390 \text{ cal/mole}$$

Expressing the partial pressures in terms of volume fractions and rearranging the form of Equation (4), the dewpoint is given by

$$T(°K) = \frac{-35{,}500}{R[\ln(V_{H_2O} V_{H_2SO_4}/C(1-C)] - 31.819} \qquad (5)$$

In order to apply Equation (5) to the prediction of dewpoints it is necessary to know the appropriate values of C as a function of vapor phase composition. Examination of the plots given by Müller indicates that the following relationship can be used at partial pressures of water vapor typical for most flue gases (ca. 0.1 atm)

$$C = 1 + 0.05 \log(V_{H_2SO_4}/V_{H_2O}) \qquad (6)$$

As indicated by this equation, and as noted by Lisle and Sensenbaugh, small variations in water vapor content do not strongly influence either the composition of the liquid phase formed or the dewpoint. This is illustrated further in Figure E-2, where the dewpoint is plotted as a function of sulfuric acid content for several water vapor concentrations.

Thus, the correlation represented by Equation (5) appears to be accurate over a wide range of vapor compositions. However, some care must be exercised in the use of Equation (6) to calculate liquid phase compositions. Equation (6) is reasonably accurate in the range of normal flue gas compositions, but does not apply at very low water contents; as the water content is lowered, additional equilibria such as the dissociation of sulfuric acid to form SO_3 must be considered.

The data presented in Figure E-2 can be used to predict the sulfuric

(2) Abel, E. "The Vapor Phase above the System Sulfuric Acid-Water", J. Phys. Chem., 50, pgs 260-283 (1946).

(3) Lisle, E. S. and Sensenbaugh J. D., "The Determination of Sulfur Trioxide and Acid Dewpoint in Flue Gases", Combustion, pgs 12-16 (January 1965)

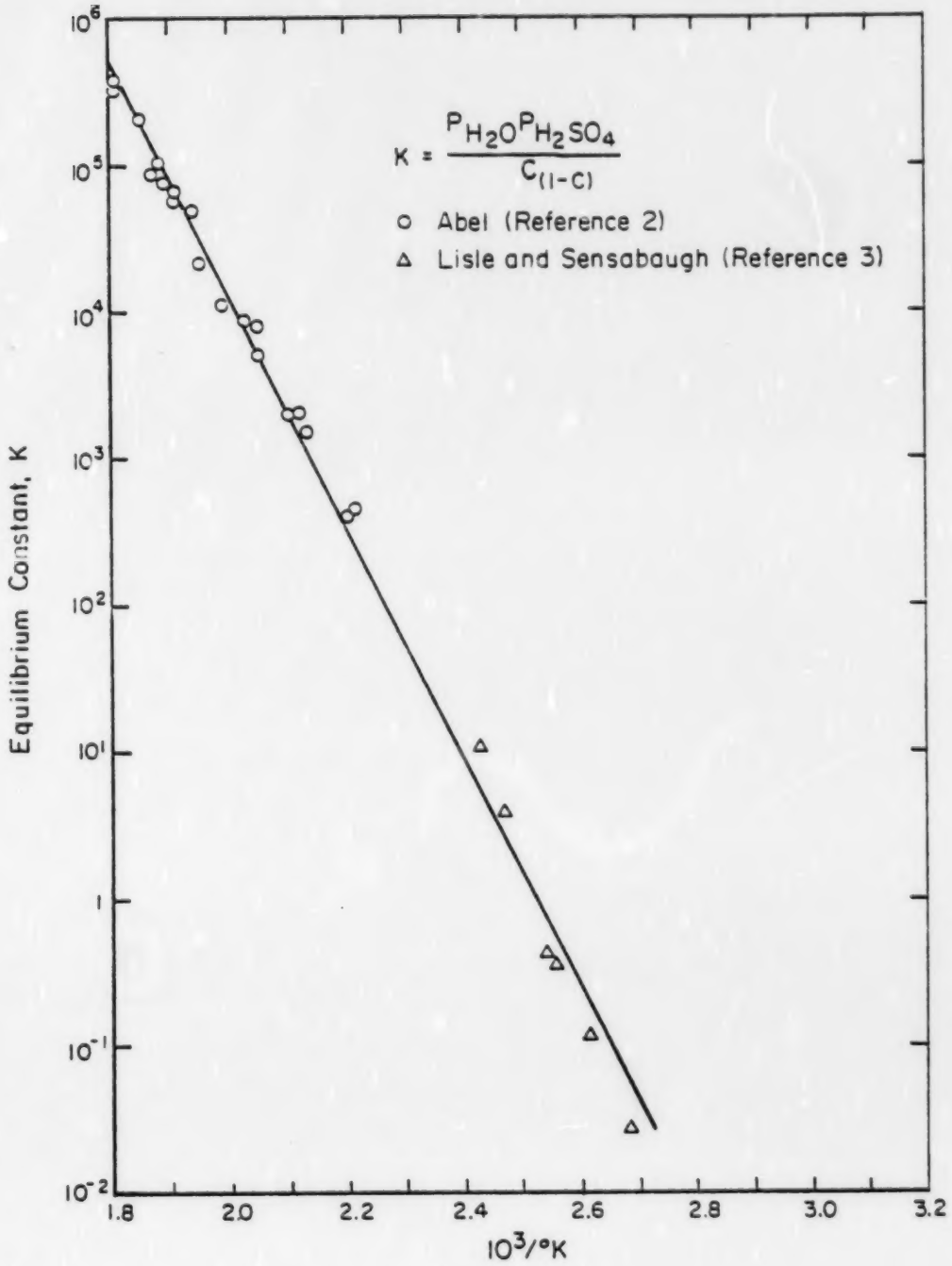

FIGURE E-1. TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANT

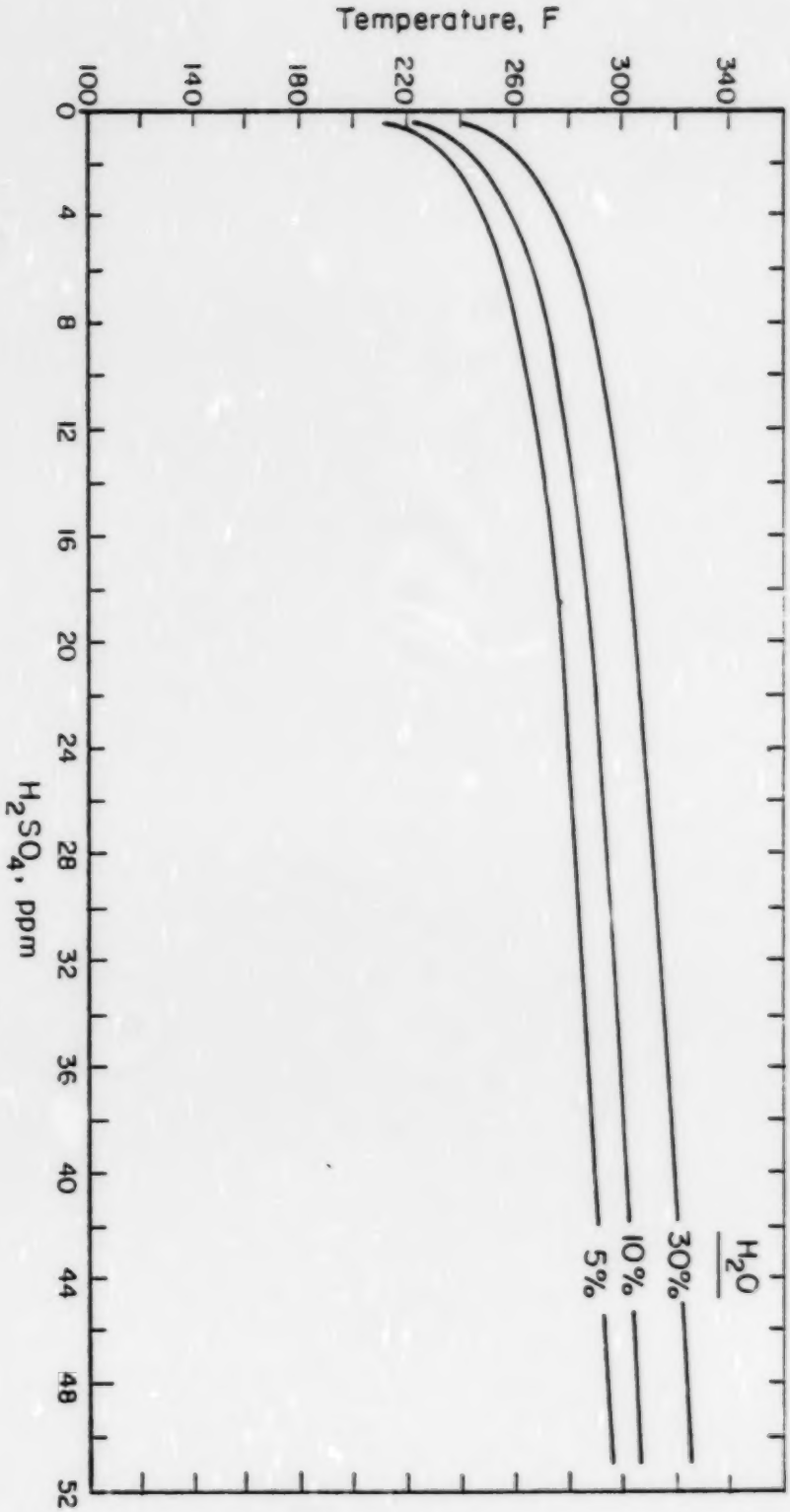

FIGURE E-2. DEWPOINT AS A FUNCTION OF SULFURIC ACID AND WATER VAPOR CONCENTRATION

acid dewpoint in cement kiln emissions. For example, the dewpoint will be about 121 C (250 F) for a sulfuric acid concentration of 4 ppm and a moisture content of 5 percent, which is typical of dry process, cement kiln emission. The dewpoint for the same sulfuric acid concentration in wet process emission with about 30 percent moisture will be about 138 C (280 F).

Ammonium Sulfate Formation

In flue gas systems containing ammonia and sulfur oxides, there is a possibility for precipitation of sulfites and/or sulfates during the sampling process. Possible compounds include $(NH_4)_2SO_3$, $(NH_4)_2SO_3 \cdot H_2O$, $(NH_4)_2SO_4$, and NH_4HSO_4. Within this group of compounds, the sulfates are much more stable than the sulfites, and the sulfites are not expected to form under normal sampling conditions unless the partial pressure of ammonia is very high. For example, $(NH_4)_2SO_3$ can be expected to form at 66 C (150 F) in flue glases containing 10^3 ppm SO_2 and 10^3 ppm NH_3. However, ammonium sulfates can form at considerably lower concentrations and higher temperatures. Figures E-3 and E-4 are nomographs showing the temperatures of precipitation of ammonium sulfate and ammonium bisulfate. Construction of these nomographs was based on thermodynamic data for the sulfates as given by Latimer[4]. As an example of the use of these plots, it can be seen that both the sulfate and the bisulfate are probable reaction products at 188-191 C (370-375 F) for flue gases containing 10 ppm NH_3 and 4 ppm H_2SO_4.

(4) Latimer, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", 2nd Edition, Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1952).

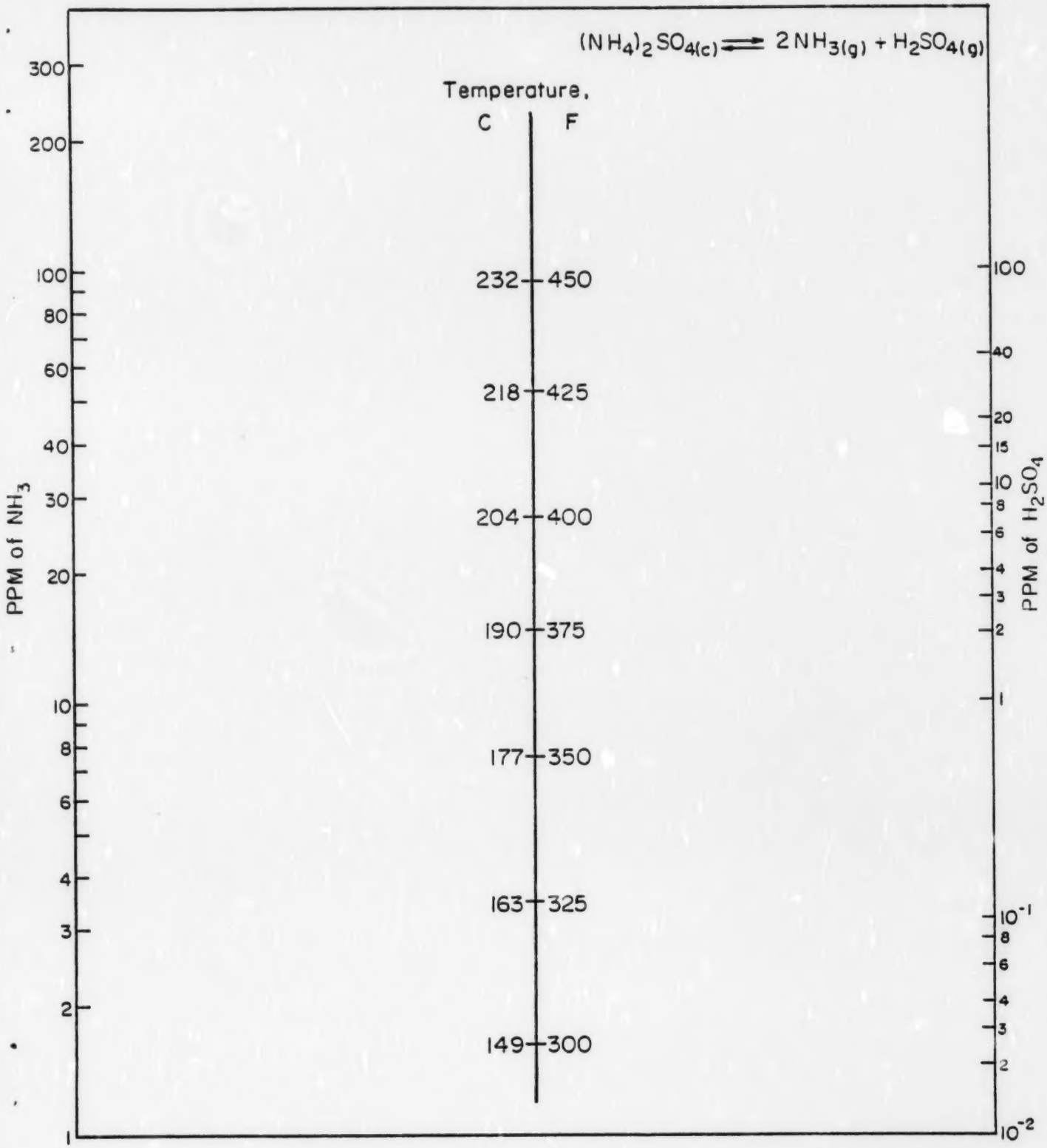

FIGURE E-3. NOMOGRAPH SHOWING TEMPERATURE OF AMMONIUM SULFATE FORMATION FOR VARIOUS AMMONIA AND SULFUEIC ACID CONCENTRATIONS

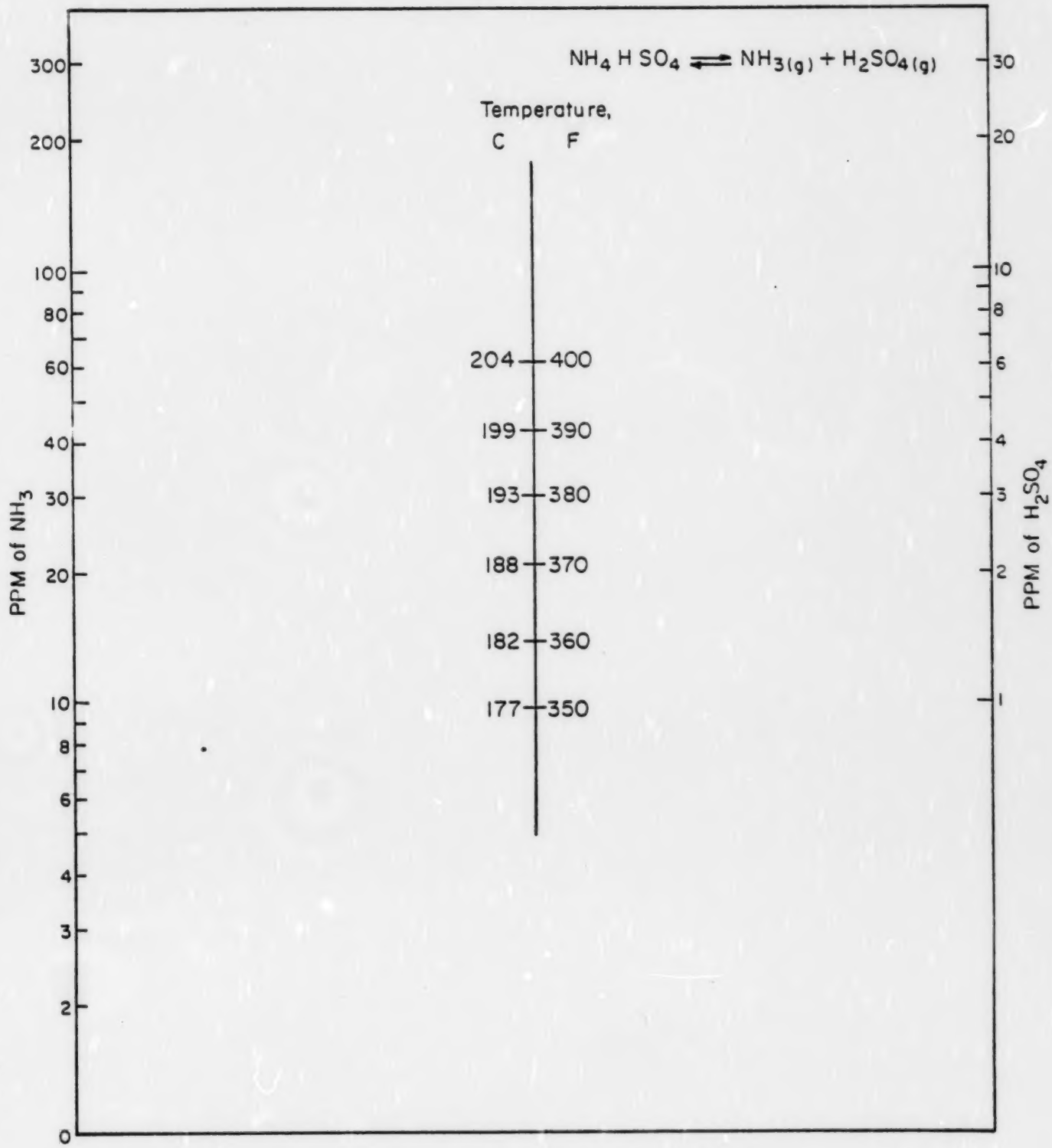

FIGURE E-4. NOMOGRAPH SHOWING TEMPERATURE OF AMMONIUM BISULFATE FORMATION FOR VARIOUS AMMONIA AND SULFURIC ACID CONCENTRATIONS